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PROCEEDINGS OF THE INTERNATIONAL LIME/LIMESTONE WET-SCRUBBING SYMPOSIUM (2ND), HELD IN NEW ORLEANS, LOUISIANA ON NOVEMBER 8-12, 1971. VOLUME II

National Environmental Research Center
Research Triangle Park, North Carolina

June 1972

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PROCEEDINGS

SECOND INTERNATIONAL
LIME/LIMESTONE
WET-SCRUBBING SYMPOSIUM

VOLUME II

November 8-12, 1971
Sheraton-Charles Hotel
New Orleans, Louisiana

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ENVIRONMENTAL PROTECTION AGENCY
Office of Administration
Research Triangle Park, North Carolina
June 1972

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Publication Number APTD-1161

PREFACE

The Second International Lime/Limestone Wet Scrubbing Symposium was held November 8-12, 1971, in the Claiborne Room of the Sheraton-Charles Hotel, New Orleans, Louisiana, sponsored by the Environmental Protection Agency, Office of Air Programs, Control Systems Division.

The Symposium, under the chairmanship and vice-chairmanship of Messrs. E.L. Plyler and D.R. Mayfield, began Monday morning with the official welcome and opening remarks by OAP's Sheldon Meyers, followed by an introduction by Mr. Plyler.

The Symposium consisted of nine sessions, divided into five different areas: fundamental research, pilot scale research and development, prototype and full scale tests, panel discussion on scaling, sampling and analytical methods.

Sessions 1 and 2, chaired by Philip S. Lowell, were concerned with fundamental research. Frank T. Princiotta of OAP was the chairman for Sessions 3 and 4 and the first three presentations of Session 5, dealing with pilot scale research and development.

The last two presentations of Session 5 and Sessions 6 and 7 were chaired by H.W. Elder. The 17 papers presented in these sessions were concerned with prototype and full scale tests.

The panel discussion on problems related to scaling in lime/limestone wet scrubbing, chaired by A.V. Slack, consisted of the five papers of Session 8. OAP's J.A. Dorsey chaired Session 9, sampling and analytical methods, which concluded the symposium early Friday afternoon.

All papers presented during the symposium are included in these proceedings except those which were given by notes and for which there exists no written text.

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MOBILE PILOT PLANT STUDY
OF THE
WET LIMESTONE PROCESS
FOR
SO_2 CONTROL

BY

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Prepared for Presentation at the
SECOND INTERNATIONAL LIME/LIMESTONE
WET SCRUBBING SYMPOSIUM

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INTRODUCTION

One of the earliest processes utilized for the removal of sulfur dioxide from combustion gases involved scrubbing with a slurry of lime or limestone in water. This process was investigated in England in the 1930's and with some significant variation has been studied since then by interested parties throughout the world. The federal government, utilities, and hardware manufacturers have recognized the potential of limestone scrubbing and are actively engaged in research and development programs to develop the process and demonstrate its commercial application.

A critical step in the commercial utilization of this process is, of course, experimentation at the pilot plant scale to develop firm data on design, operation, and economics and to re-examine laboratory data in a more realistic environment. The pilot plant stage allows a more critical review of factors such as process chemistry, mass transfer mechanisms, scale formation and control, effect of limestone characteristics, optimum scrubber design, and identification of water pollution problems.

Zurn Industries, Incorporated along with the Office of Air Programs, Environmental Protection Agency conducted a joint research project which involved a pilot plant study of wet limestone scrubbing utilizing a Zurn Air Systems Division

"Dustraxtor" scrubber. The pilot plant was mobile and was installed at two electric generating stations, an oil-fired station in Key West, Florida and a coal-fired station in Paducah, Kentucky. The study was applied in nature and investigated variables important to the success of the limestone scrubbing process. Data were developed which will ultimately be utilized in a demonstration project to be discussed later during this symposium. Since Zurn Industries has an interest in the commercial development of this type of system, we contributed significantly to the cost of the project through the design and construction of the pilot plant.

CHEMICAL CONTACTING IN THE DUSTRAXTOR

The objective of flue gas scrubbing for mass transfer is to remove as much material as economically possible out of the gas and into the scrubbing liquid. There are physical, chemical equilibrium, and rate relationships that limit the solubility of material in liquid that control the mass transfer relations. However, the amount of mass transfer not only depends upon the equilibrium relationships, but also on the contacting scheme. The "Dustraxtor" employs many contacting schemes in its operation.

The "Dustraxtor" scrubbing unit employed in the pilot plant study is a type of turbulent contact scrubber and is shown in Figures 1 and 2. The unit consists of a flooded, collecting tube through which the flue gas must pass. The collecting tube is installed vertically in the inlet plenum chamber directly above the recycle hopper so that the bottom of the tube is a short distance above the liquid level in the hopper.

Flue gases enter the inlet plenum chamber where they sweep over the surface of the scrubbing liquid and are directed up the collecting tube. The velocity of the gas passing beneath the collecting tube and above the collecting bonnet draws the scrubbing slurry from the bonnet surface and upward into the collecting tube. The shearing action of the gas atomizes the scrubbing slurry into a dense spray as the gas-slurry mixture continues up through the collecting tube. The result of this action is a highly turbulent mixing zone which provides the intimate contacting and time necessary for the chemical reaction to occur. As the gases are discharged from the collecting tube, they are directed into a curved liquid deflector which acts as a separator by forcing the slurry downward onto the tube sheet. This shower effect provides an additional mixing zone for absorption with chemical reaction to occur. The cleaned gas is discharged through the exhaust stack and the scrubbing solution is returned by gravity to the recycle hopper. When employed for limestone scrubbing, this built-in recycle of the scrubbing slurry provides sufficient time for the limestone to go into solution and react with the sulfur oxides.

The stages of contact in this type of unit are:

1. The initial shearing action as the flue gas passes through the slot between the collecting bonnet and tube.
2. The highly turbulent mixing zone within the collecting tube where the gas is in intimate contact with liquid droplets.
3. Impingement of the gases and liquid upon the surface of the deflector.

4. The passage of the gas through a highly turbulent curtain of liquid being discharged from the liquid deflector.

The contacting schemes found in this type of unit include counter-current, co-current, and cross-current. Since there are many contacting schemes taking place at the same time in this unit, a theoretical analysis of the total mass transfer mechanism would be very complicated to perform and may prove to be only of academic interest.

The unit normally operates at a pressure drop of from 6 to 8 inches WG. This pressure drop is regulated by either raising or lowering the adjustable level control weir. One advantage of this type of unit in limestone scrubbing applications is that there are no moving parts, spray nozzles, or pumps necessary for operation. By variation in weir height, bonnet spacing or tube selection, a wide range of operating conditions may be met at maximum efficiency.

DESCRIPTION OF THE MOBILE PILOT PLANT

Zurn Industries cooperated with the Office of Air Programs, Environmental Protection Agency on a project in which a mobile limestone scrubbing pilot plant was designed, manufactured, and operated. The major objectives of the pilot plant study were to evaluate the potential of this type of turbulent contact scrubber in the wet limestone process, investigate process chemistry and kinetics, and generate design data for scale-up purposes. The first phase of the pilot plant study was conducted in Key West, Florida, at the municipal power plant which burned approximately 1-2 percent sulfur content fuel oil. After this phase of the project was completed, the mobile pilot plant was moved to the TVA Shawnee coal-fired power plant for the second phase of the study.

Figure 3 is a schematic flow diagram of the pilot plant. The scrubber had a nominal capacity of 1500 cfm. The dry collector permitted operation with and without fly ash when used during the second phase of the study. Other salient features of the pilot plant were capabilities to handle a wide range of gas and liquid flow rates, construction materials to withstand a wide range of pH (pH 3 to 9), and provisions for ready access to the scrubber to check on scale buildup and for scale removal, if necessary.

Six types of limestone reactants were evaluated (coral marl, aragonite, Fredonia Valley limestone, dolomite, precipitated calcium carbonate, and lime). A background series of tests were conducted with salt water. The stoichiometry of the reactant and the effect of slurry concentration were studied for selected limestones. Stoichiometric requirements were based upon the molar requirements for the reactant to form $CaSO_3$. For selected reactants, the influence of particle size on sulfur dioxide removal efficiency was studied. The effect of an iron catalyst on sulfur dioxide removal efficiency and on the composition of the spent liquid slurry was also evaluated.

The scrubber variables evaluated with respect to the efficiency of sulfur dioxide removal for the most effective reactant combinations include gas flow rate, system pressure drop, stoichiometry, particle size, and slurry concentration. Other factors analyzed during the test program included but were not limited to:

Corrosion of the various metals utilized throughout the system.

Scale formation.

Operating and maintenance problems associated with operation of the system.

In order to evaluate these variables, the following data were collected during each experimental run:

Boiler operating conditions.

Inlet and outlet gas samples including sulfur oxides, nitrogen oxides, particulates, flow rate, temperatures (wet bulb and dry bulb).

Compositions of the slurry feed to scrubber and scrubber slurry discharge including solids concentration, calcium and magnesium, sulfate and sulfite, nitrogen compounds, chloride, pH. temperature, and flow rate.

The equipment utilized for this study included a modified Dustraxtor containing one tube. The scrubber was modified by the addition of an external weir to enable measurement of the quantity of liquid drawn up the tube. The scrubber was designed such that various tube diameters could be tested in the system. (12 inch I.D. and 8 inch I.D. tubes were utilized during this study). A continuous record of the inlet and outlet sulfur dioxide concentration was taken during each experimental run utilizing a Dynasciences Model SS-130 analyzer connected to a strip chart recorder. The analyzer was calibrated twice daily utilizing a known standard of certified calibration gas. Intermittent nitrogen oxide and particulate samples were taken utilizing standard stack sampling techniques and analyzed with standard procedures. Gas flow rate was determined with a calibrated "Annubar" flow meter.

The mobile pilot plant was installed on the Number 3 unit of the Key West Municipal Power Plant during the first phase of this study. This unit has a generating capacity of 20 MW and was burning 1 to 2 percent sulfur content fuel oil during the experimental period. During the second phase of this study, the mobile pilot plant was installed on the Number 9 and 10 units of TVA's Shawnee generating station. Each unit has a generating capacity of 150 MW and was burning 2½ to 4 percent sulfur content coal during the experimental period. The Number 10 unit at the Shawnee plant was also in the dry limestone injection configuration and this gas was scrubbed in the mobile pilot plant.

RESULTS OF THE TEST PROGRAM

This section of the report will discuss the results from the three major phases of the test program as well as operating and maintenance problems associated with the pilot plant. Generally speaking, the pilot plant performed satisfactorily with only the normal problems that might be expected in this type of operation.

A detailed final report on this project is currently being prepared and will be available soon. This presentation will only summarize some of the tests conducted on an oil-fired boiler, a coal-fired boiler, and a limestone-injection boiler. The results were favorable and indicate that this type of scrubber should be considered for use in the wet limestone SO_2 control process.

Key West Tests

Initial tests were conducted at the Key West site to determine the quantity of liquid that was drawn up into the tube. Figure 4 summarizes the data accumulated during this phase of the test program. As can be seen from Figure 4, the quantity of liquid drawn up into the tube is a function of the gas flow rate and pressure drop across the scrubber. Liquid to gas ratios of 100 to greater than 500 gallons per MCFM were attainable with this scrubber configuration.

Figure 3 illustrates the scrubber configuration and sample locations utilized during the limestone scrubbing phase of the Key West test program. A fractional factorial design was employed to determine the major parameters which effect SO_2 removal in this type of scrubber. Tables 1 and 2 summarize the field test data associated with the experimental design for each primary reactant, coral and Fredonia Valley limestone. Based upon the experimental design, stoichiometry, gas flow rate and pressure drop are highly significant factors in the design of a SO_2 -limestone scrubbing system using this type of scrubber. Figure 5 summarizes the results obtained with the two primary reactants studied. Generally, at a stoichiometric ratio of 1:1, a pressure drop of 6.5 inches H_2O, and 2000 ACFM gas flow rate, efficiences of 50-75 percent were attained depending upon the grind of the reactant studied. An increase in scrubber pressure drop to 12 inches H_2O and a decrease in gas flow rate to 1000 ACFM improved removal efficiency to a level of 75 to 90 percent. However, it should be pointed out that the scrubber was in a once-through configuration and was only operated for a period of 3 to 4 hours per test.

Figure 6 summarizes the effect of pH upon SO_2 removal efficiency during this phase of the test program. Due to the location of the fresh slurry feed line, in relation to the spent slurry discharge, improper mixing occurred in the scrubber, and the discharge pH was not as reliable an indicator of this effect as the weir pH.

Another test series was conducted to determine the effect of gas flow rate upon SO_2 removal efficiency. The test conditions were fixed, and only the gas flow rate through the scrubber was varied. Figure 7 summarizes the results obtained during this series of tests. The results were as expected, when the L/G ratio for a given tube diameter increased, the SO_2 removal efficiency increased. The liquid flow rate utilized in the L/G calculation is actually the liquid drawn up into the tube based upon Figure 4 and not the actual liquid flow to the scrubber.

Tests were conducted using other reactants, dolomite, lime, and precipitated calcium carbonate. The results of this phase of the test program are summarized in Table 3. All reactants ran satisfactorily except for precipitated calcium carbonate which caused heavy foaming at the weir and inside the scrubber.

Shawnee Unit No. 9 Tests

Table 4 summarizes the Fredonia Valley limestone tests conducted while the mobile pilot plant was connected to the No. 9 unit at the Shawnee station. Due to pressure drop consideration across the entire system, it was necessary to conduct all tests with an 8 inch diameter tube. A fractional factorial design similar to that used during the first phase of the test program was utilized for the primary reactant. Commercially available grinds were used to determine the effect of particle size on SO_2 removal efficiency. Each experiment was conducted with the primary dust collector in operation as depicted in Figure 3. The experimental technique was identical to that utilized in Key West, wherein the liquor fed to the scrubber was based upon the test stoichiometry, gas flow rate and SO_2 concentration in the entering gas. Figure 8 summarizes the results from this test series. The highly significant parameters for this system were found to be pressure drop, gas flow rate, and stoichiometry. Particle size was not a significant factor due to the large amount of 100 mesh material passing the 325 mesh screen. This situation occurred in previous studies and made it very difficult to determine the effect of a coarser grind upon SO_2 removal efficiency.

During testing on No. 9 unit, little or no mechanical or operating difficulties were encountered. Scale formation was not a problem due to the installation of a device to continually wash down the tube. Based upon the limited number of tests and operating hours on a coal-fired unit, removal efficiencies of 35 to 80 percent may be expected in a once-through configuration depending upon gas flow rate, stoichiometry, particle size and pressure drop. However, additional testing would be required prior to any large scale-up of this scrubber for control of SO_2 from a coal-fired station.

An abbreviated test series was conducted inorder to evaluate the effect of ionic strength upon SO_2 removal. A increased ionic strength slurry solution was tested at a similar pressure drop, gas flow rate and stoichiometry as was used during the first phase of this study. The results are shown below:

Location	SO_2 Removal Efficiency %
No. 9 Unit	69.6
No. 9 Unit, Simulated Ionic Strength (12,000mg/l Cl^-)	75.5
Key West (24,000 mg/l Cl^-)	84.2

Shawnee Unit No. 10 Tests

Figure 9 illustrates the configuration of the mobile pilot plant when installed on the No. 10 unit at Shawnee. All gas to the scrubber, laden with calcined limestone from the limestone injected boiler, by-passed the primary mechanical collector and entered the scrubber. Table 5 summarizes the results from this test series. As can be seen, SO_2 removal efficiencies of 60 to 94 percent were attainable depending upon stoichiometry, gas flow rate, and pressure drop. However, due to the design of the scrubber, the entering gas and limestone impinged upon the tube and built-up until the cake fell off due to its weight. A re-design of the entrance to the scrubber would be necessary before this unit could be applied on a limestone injection boiler. The low inlet SO_2 concentrations found during this test program can be attributed to leakage of ambient air into the system.

Operating Problems

In addition to the operating problems discussed previously, two other problems were associated with the mobile pilot plant: corrosion and scale build-up on the blower. Since the scrubber was initially tested utilizing salt water, severe corrosion problems occurred in the scrubber and discharge piping. However, once the salt water tests were concluded and fresh water was utilized in the system, no additional failures due to corrosion were encountered.

Scale build-up on the blower blades caused serious operating problems more than once during the life of this project. The scale build-up would occur on the blower blades, causing an imbalance in the system, and in some cases, ultimate failure of the blower. This problem could have been avoided by using a "hot-side" blower instead of locating one down-stream of the scrubber system.

Scale Formation in the Scrubber

Scale formation occurred at two points in the scrubber system. Initially, scale was discovered at the tip of the tube in an area of high turbulence and then at a later date, some slight crystal formation was noticed on the scrubber housing at the water line. Heavy scale formation on the tube lip could develop into an operating problem if not corrected, since the crystal growth occurred directly in the gas path; therefore, precautions were taken to eliminate scale formation at this location. Table 6 indicates the major compounds found in a sample of the scale formed on the tube.

TABLE 6

ANALYSIS OF TUBE SCALE

Compound	Quantity (wt %)
$CaSO_4 \cdot 2H_2O$	30.5
$CaCO_3$	68.0
$MgCO_3$	1.5

Rate of scale formation appeared to be a direct function of the slurry concentration; however, no effort was made to quantify this conclusion. An appreciable difference was not noticed in the rate of scale formation caused by the primary reactants tested, coral or Fredonia Valley limestone.

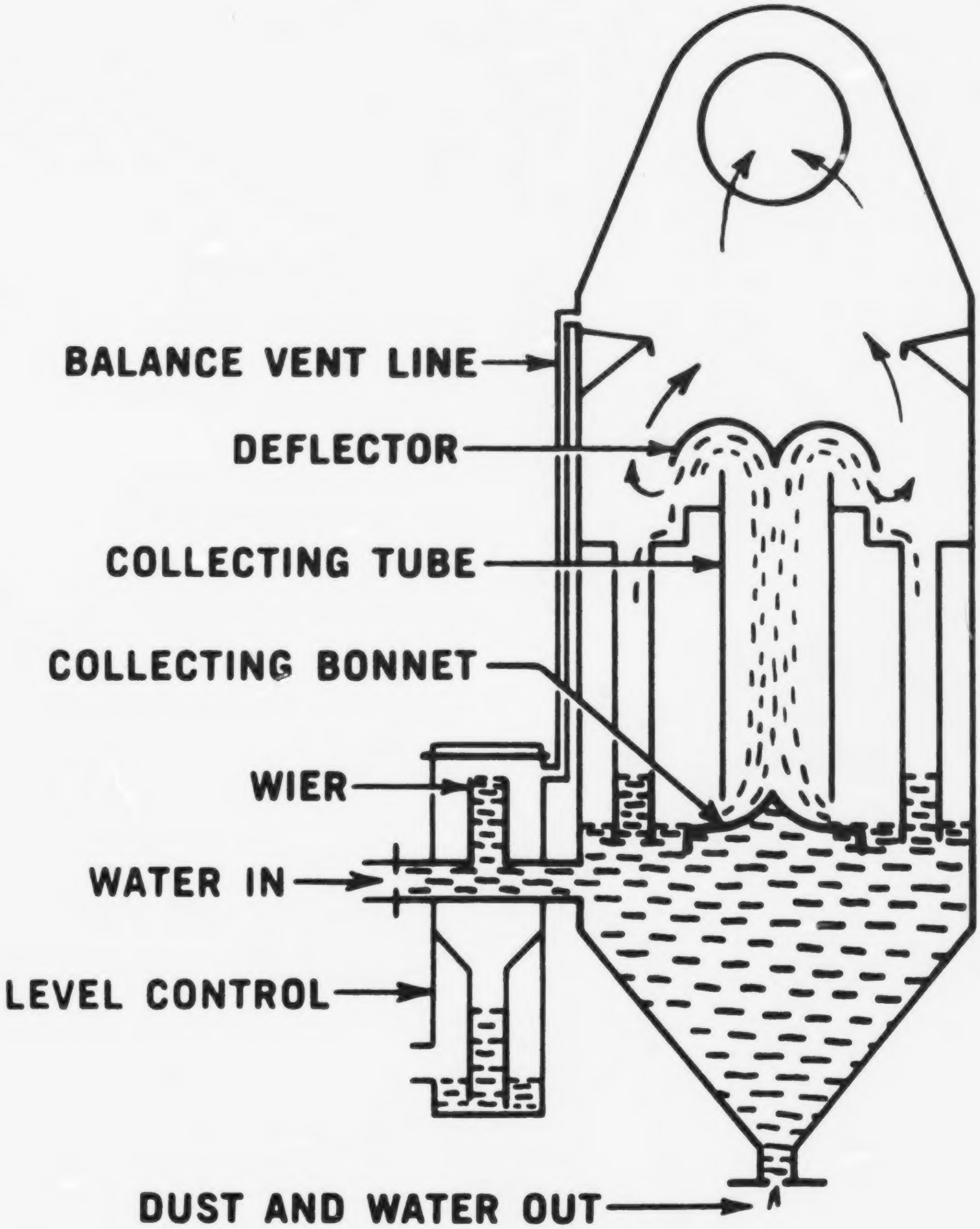


FIGURE 1. TYPICAL CROSS SECTION OF DUSTRAXTOR

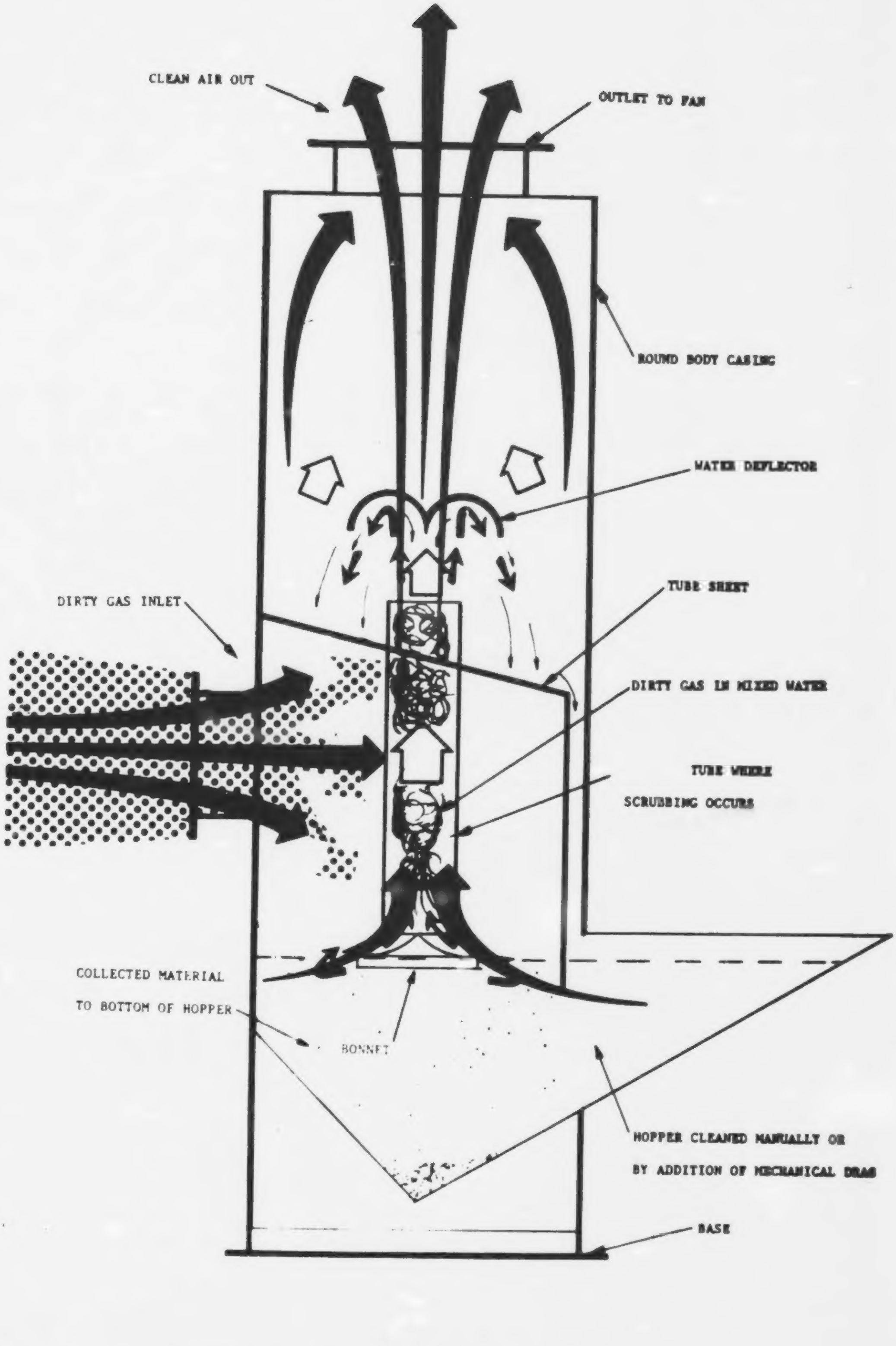
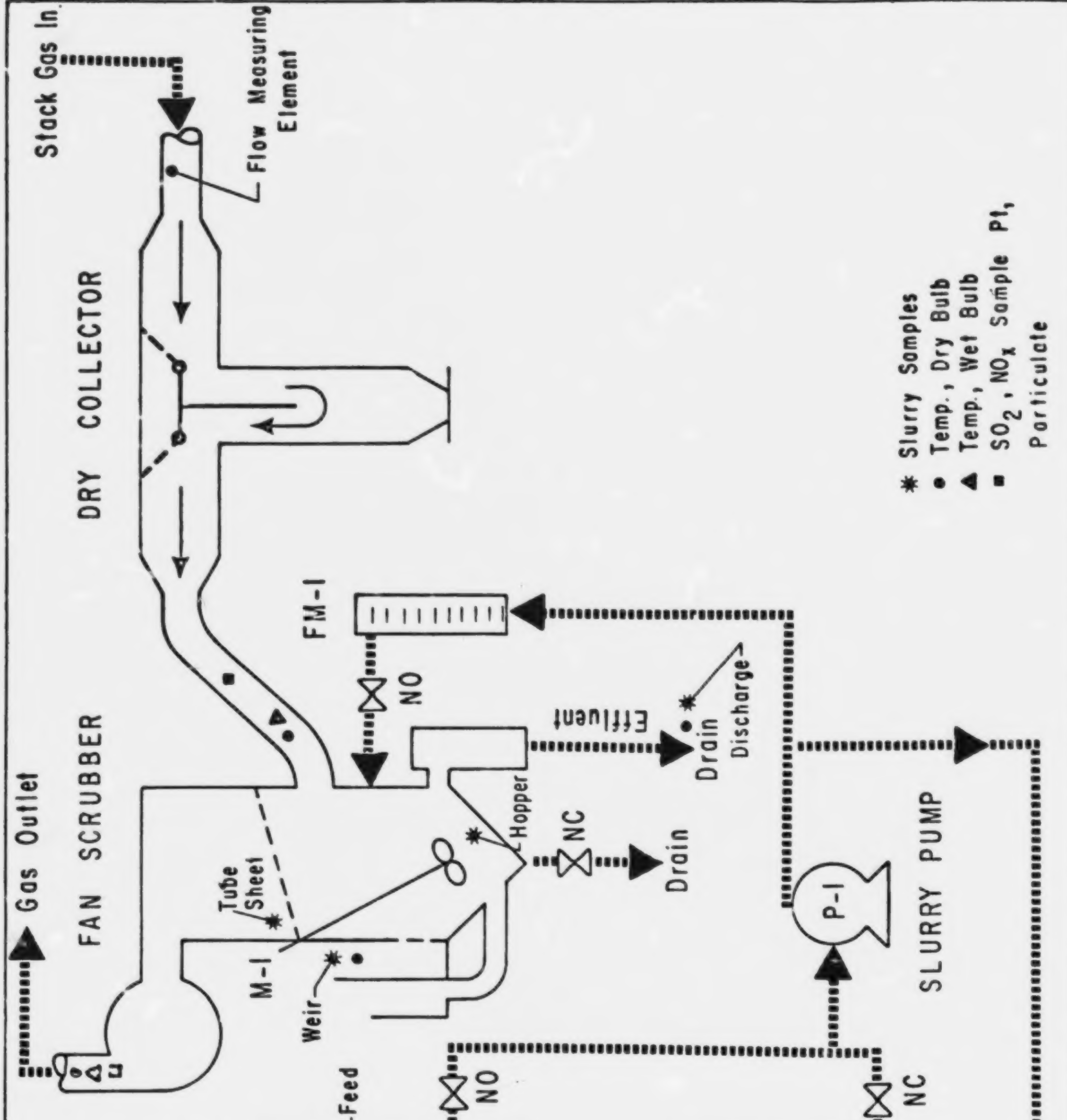

CLEAN AIR OUT
OUTLET TO FAN
ROUND BODY CASING
WATER DEFLECTOR
TUBE SHEET
DIRTY GAS INLET
DIRTY GAS IN MIXED WATER
TUBE WHERE SCRUBBING OCCURS
COLLECTED MATERIAL TO BOTTOM OF HOPPER
BONNET
HOPPER CLEANED MANUALLY OR BY ADDITION OF MECHANICAL DRAG
BASE

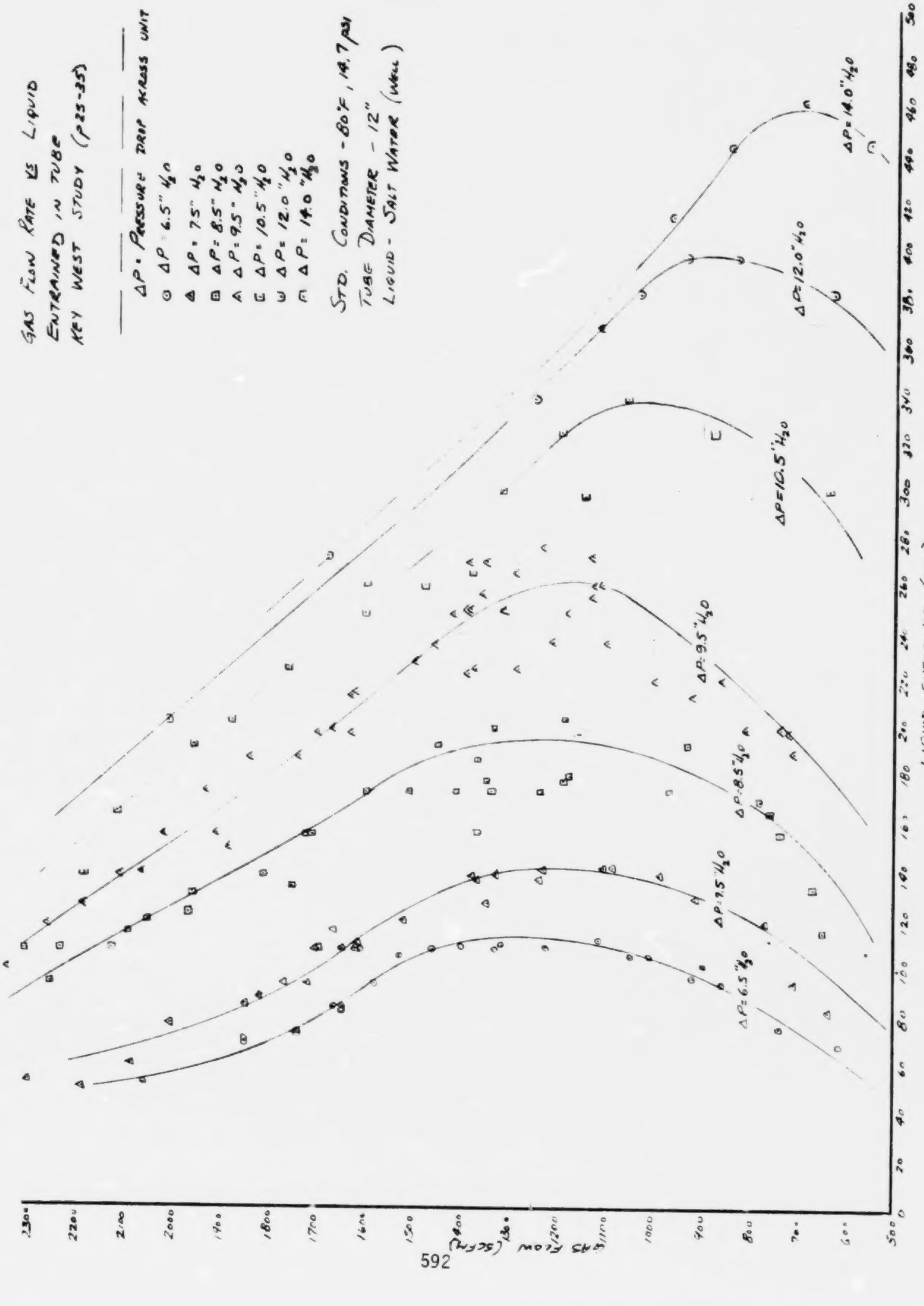
FIGURE 2. DIAGRAMMATIC VIEW OF SCRUBBING ACTION WITHIN DUSTRAXTOR



Stack Gas In
Flow Measuring Element
DRY COLLECTOR
FAN SCRUBBER
Gas Outlet
Tube Sheet
M-1
Weir
Hopper
NC
Drain
FM-1
NO
Effluent
Drain
Discharge
P-1
SLURRY PUMP
Feed
Reactant & Feed Water
NO
NC
M-2
T-1
MIX TANK
Drain
M-3
T-2
MIX TANK
* Slurry Samples
● Temp., Dry Bulb
▲ Temp., Wet Bulb
■ SO_2, NO_x Sample Pt, Particulate

FIGURE 3

FIGURE 4



GAS FLOW RATE VS LIQUID ENTRAINED IN TUBE KEY WEST STUDY (P25-35)
ΔP = PRESSURE DROP ACROSS UNIT
⊙ ΔP = 6.5" H2O
△ ΔP = 7.5" H2O
⊡ ΔP = 8.5" H2O
∧ ΔP = 9.5" H2O
E ΔP = 10.5" H2O
⊍ ΔP = 12.0" H2O
∩ ΔP = 14.0" H2O
STD. CONDITIONS - 80°F, 14.7 psi
TUBE DIAMETER - 12"
LIQUID - SALT WATER (WELL)
ΔP = 6.5" H2O
ΔP = 7.5" H2O
ΔP = 8.5" H2O
ΔP = 9.5" H2O
ΔP = 10.5" H2O
ΔP = 12.0" H2O
ΔP = 14.0" H2O
LIQUID ENTRAINED (GPM)
GAS FLOW (SCFM)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
2100
2200
2300

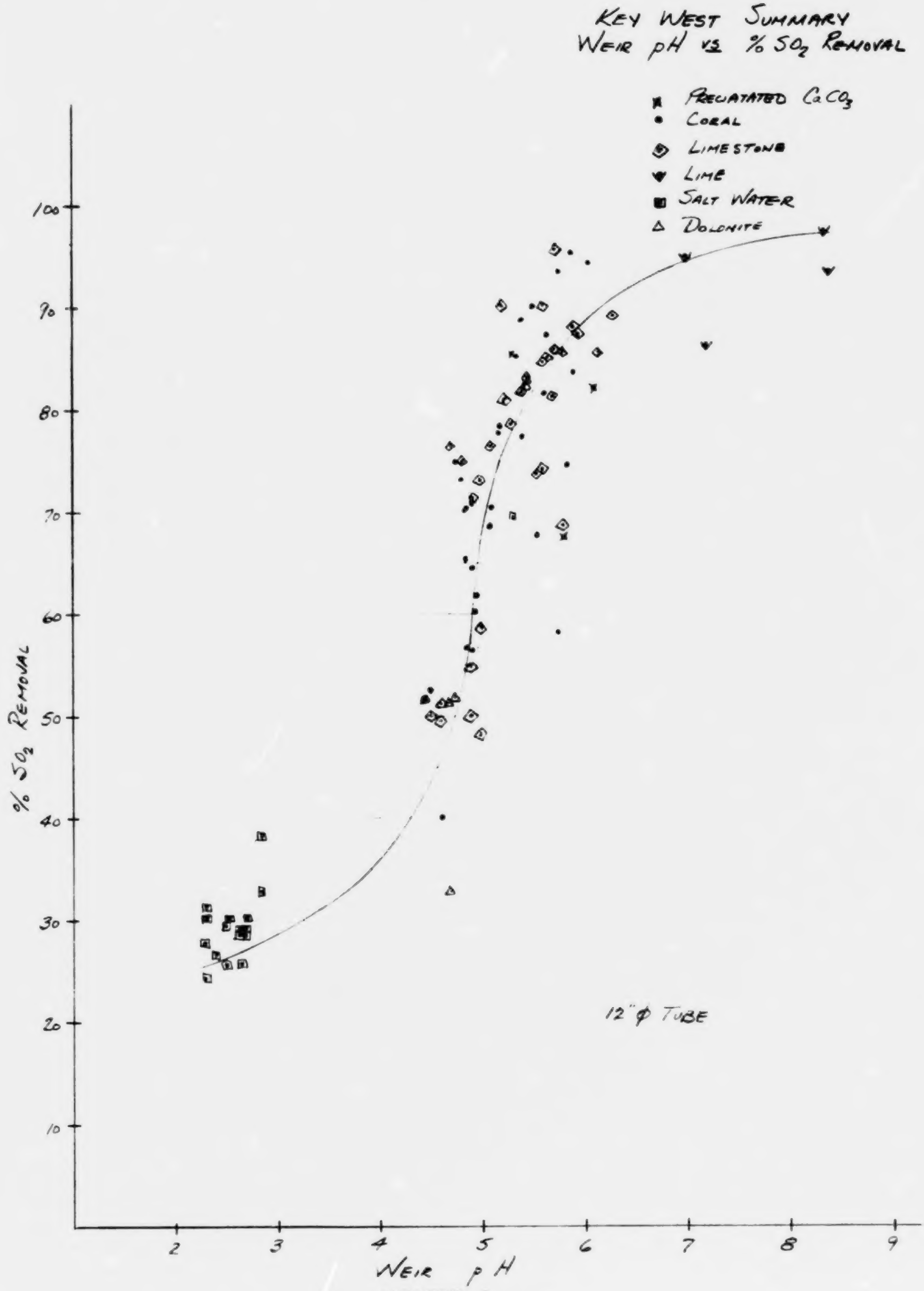

KEY WEST SUMMARY
WEIR pH vs % SO2 REMOVAL
PRECIPITATED CaCO3
CORAL
LIMESTONE
LIME
SALT WATER
DOLOMITE
12" φ TUBE
% SO2 REMOVAL
100
90
80
70
60
50
40
30
20
10
2
3
4
5
6
7
8
9
WEIR pH

FIGURE 5

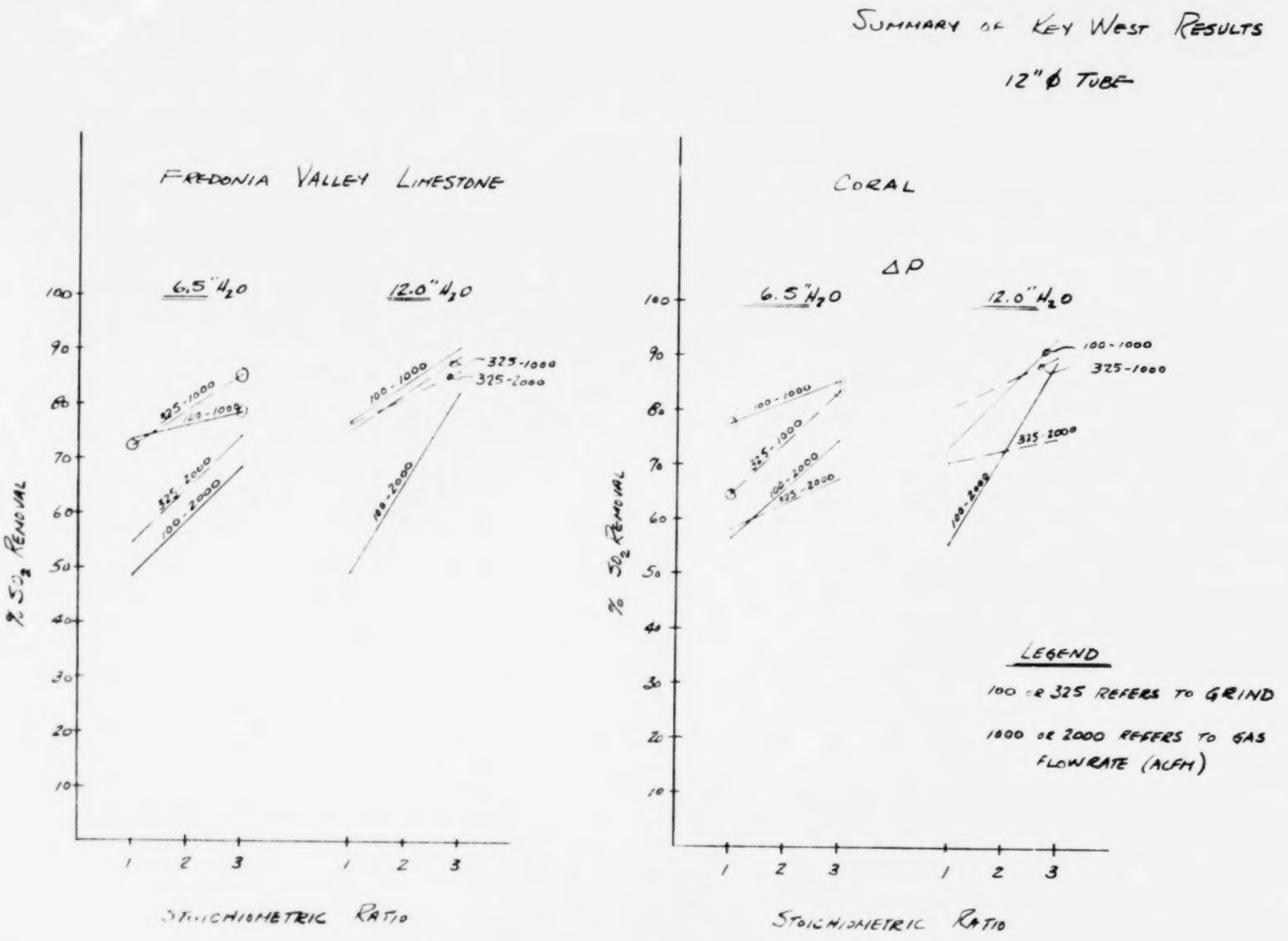

Summary of Key West Results
12" ø Tube
Fredonia Valley Limestone
Coral
ΔP
6.5" H2O
12.0" H2O
6.5" H2O
12.0" H2O
% SO2 Removal
% SO2 Removal
100
90
80
70
60
50
40
30
20
10
1
2
3
325-1000
100-1000
325-2000
100-2000
100-1000
325-1000
325-2000
100-2000
Stoichiometric Ratio
Stoichiometric Ratio
Legend
100 or 325 refers to grind
1000 or 2000 refers to gas flowrate (ACFH)

FIGURE 6

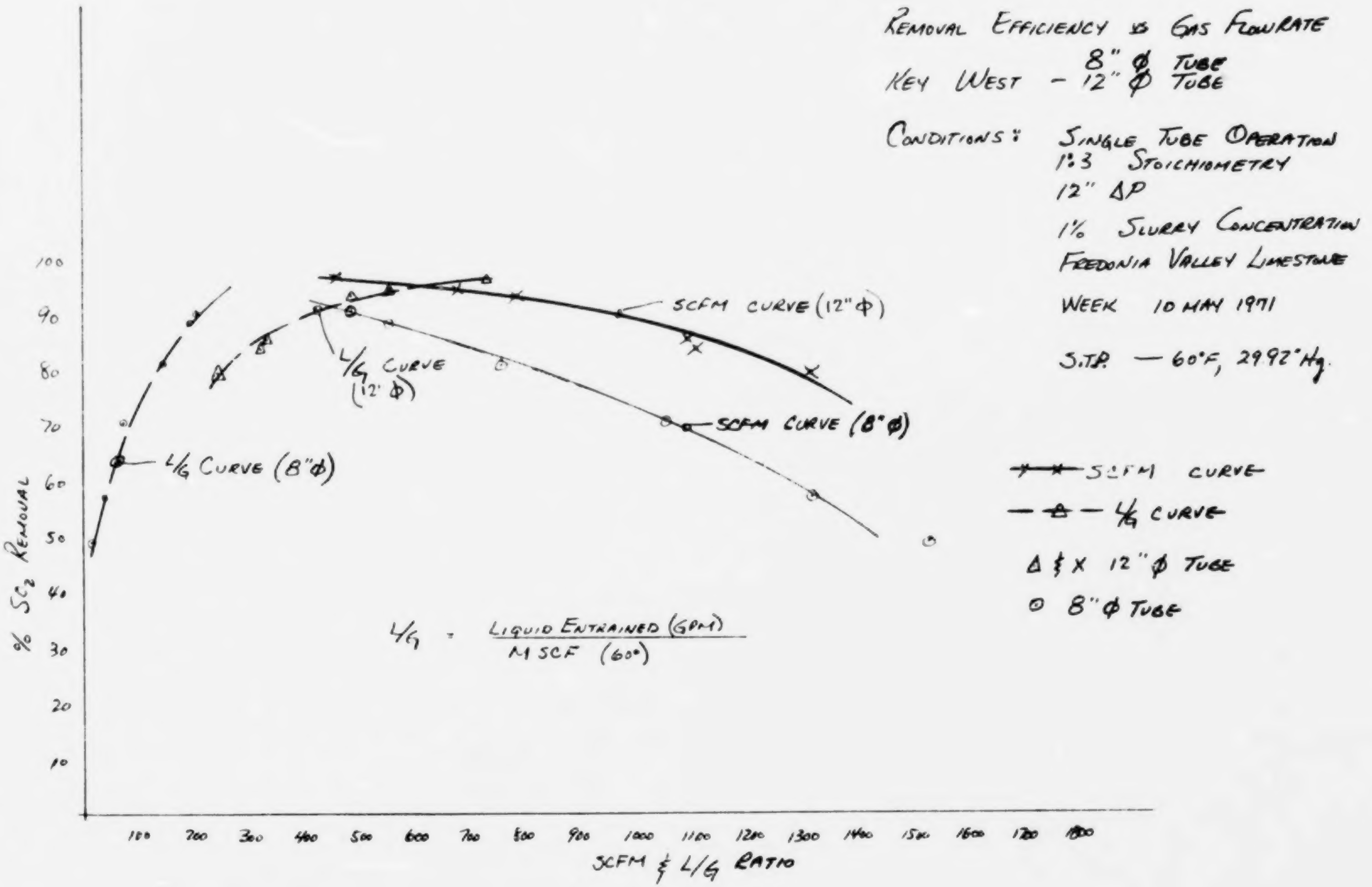

REMOVAL EFFICIENCY vs GAS FLOWRATE
KEY WEST - 8" ϕ TUBE
12" ϕ TUBE
CONDITIONS: SINGLE TUBE OPERATION
1:3 STOICHIOMETRY
12" ΔP
1% SLURRY CONCENTRATION
FREDONIA VALLEY LIMESTONE
WEEK 10 MAY 1971
S.T.P. — 60°F, 29.92" Hg.
SCFM CURVE (12" ϕ)
SCFM CURVE (8" ϕ)
L/G CURVE (12" ϕ)
L/G CURVE (8" ϕ)
SCFM CURVE
L/G CURVE
Δ & X 12" ϕ TUBE
⊙ 8" ϕ TUBE
L/G = LIQUID ENTRAINED (GPM) / M SCF (60°)
% SO2 REMOVAL
100
90
80
70
60
50
40
30
20
10
SCFM & L/G RATIO
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800

FIGURE 7

SUMMARY OF PADUCAH TEST SERIES

REACTANT: FREDONIA VALLEY LIMESTONE

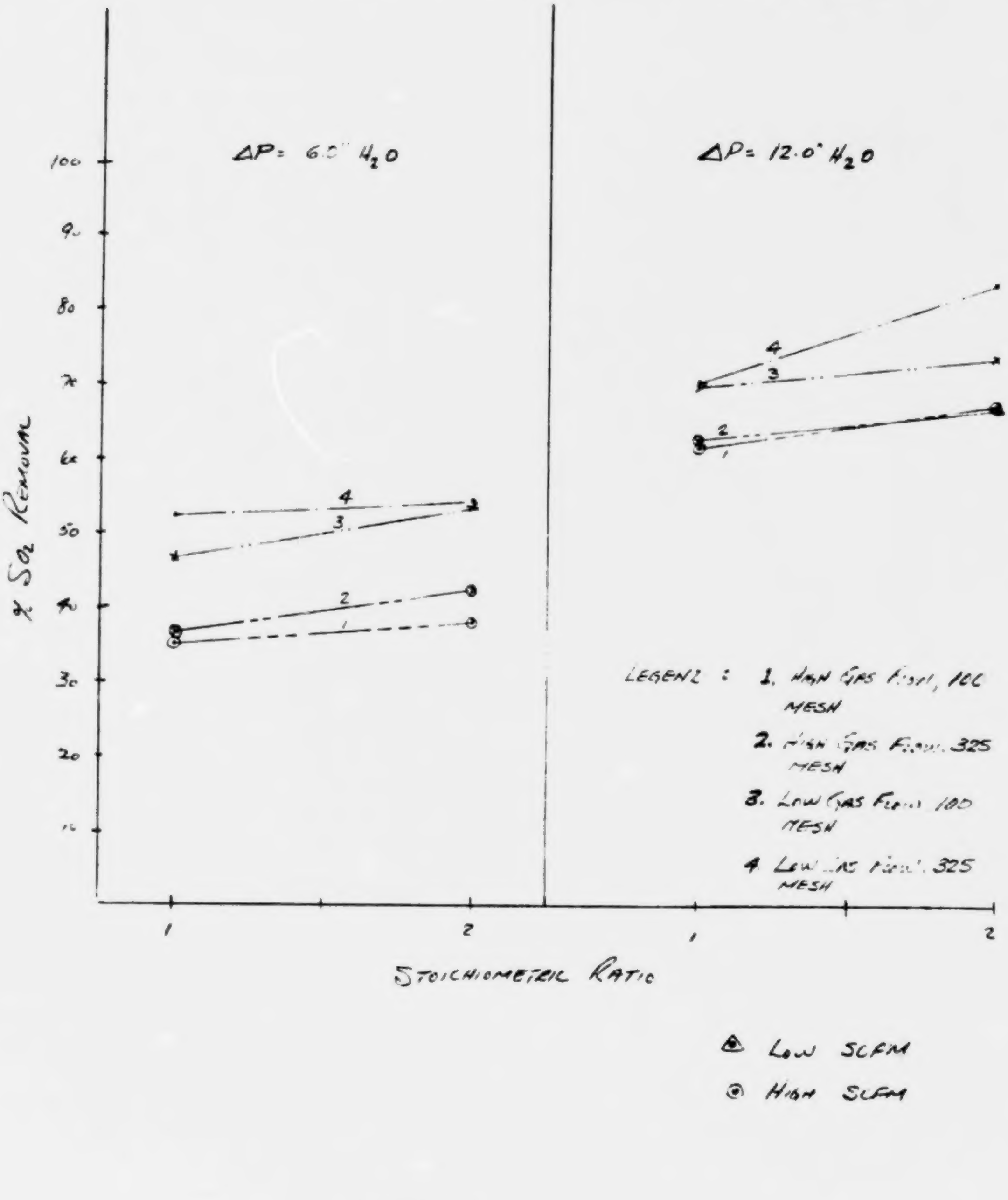


FIGURE 8

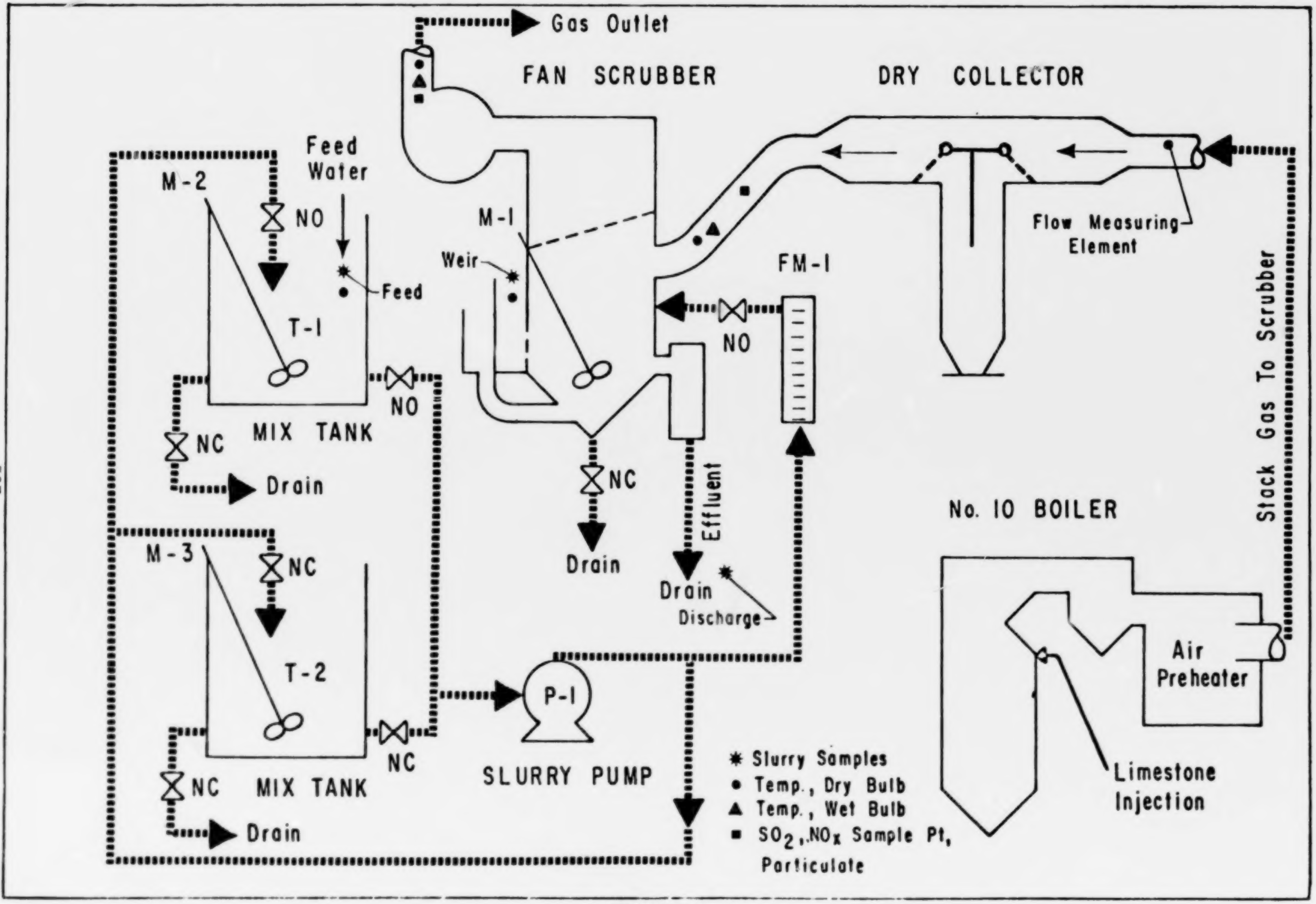

Gas Outlet
FAN SCRUBBER
DRY COLLECTOR
Feed Water
M-2
NO
Feed
T-1
M-1
Weir
Flow Measuring Element
FM-1
NO
NO
NC
MIX TANK
NC
Drain
Drain
Effluent
Drain
Discharge
No. 10 BOILER
Stack Gas To Scrubber
M-3
NC
T-2
P-1
NC
NC
MIX TANK
SLURRY PUMP
Drain
Air Preheater
Limestone Injection
✱ Slurry Samples
● Temp., Dry Bulb
▲ Temp., Wet Bulb
■ SO2, NOx Sample Pt, Particulate

FIGURE 9

TABLE 1

SUMMARY OF KEY WEST FRACTIONAL FACTORIAL DATA

Coral FIELD TEST DATA (12"Φ TUBS)

Test Number	C-14	C-28	C-8	C-19	C-20	C-7	C-29	C-15	C-21	C-18	C-23	C-17	C-16	C-24	C-13	C-22
Test Conditions																
Gas Flowrate (scfm)	1470	788	775	1465	794	1478	1445	771	794	1478	1483	772	1452	788	721	1457
Pressure Drop (in. H_2O)	12.0	6.5	6.5	6.5	6.5	12.0	12.0	6.5	12.0	6.5	6.5	12.0	6.5	12.0	12.0	6.5
Stoichiometric Ratio	1:3	1:1	1:1	1:1	1:3	1:1	1:1	1:3	1:1	1:3	1:3	1:1	1:1	1:3	1:3	1:1
Slurry Concentration (wt. %)	5	5	1	1	1	1	5	5	1	1	5	5	5	5	1	1
Particle Size	325	100	325	325	100	325	100	325	100	325	100	325	325	100	325	100
Gas Conditions																
Entering																
Temperature (T_{db})	248	215	206	227	204	248	246	222	200	227	242	218	256	215	238	240
Temperature (T_{wb})	134	128	130	128	125	133	130	128	125	127	130	131	134	128	132	130
SO_2 Concentration (ppm)	960	770	415	715	735	436	750	960	735	920	800	980	980	750	690	815
NO_x Concentration (ppm)	—				—			—	—	—	—	—	—	—	—	—
Leaving																
Temperature (T_{db})	132	140	140	110	124	131	130	143	128	132	140	142	148	136	135	141
Temperature (T_{wb})	128	124	125.	116	112	128	127	126	116	116	124	127	130	124	120	123
SO_2 Concentration (ppm)	240	166	147	80	108	128	333	155	198	298	203	191	410	50	68	355
NO_x Concentration (ppm)	—				—			—	—	—	—	—	—	—	—	—
Slurry Conditions																
Flowrate (gpm)	2.60	0.40	1.10	9.90	5.40	2.00	0.70	1.30	1.80	13.00	2.20	0.45	0.90	1.10	4.75	3.60
Temperature																
Feed (°F)	80	77	76	76	74	78	77	80	75	76	77	83	81	78	80	76
Effluent (°F)	126	121	121	114	112	124	125	122	116	110	122	120	124	120	120	122
pH																
Feed	7.70	7.65	7.90	7.55	7.55	7.80	7.80	7.70	7.60	7.80	7.55	7.90	7.80	7.60	7.65	7.55
Effluent	4.80	5.55	5.10	5.60	5.45	5.15	4.62	6.10	4.85	5.70	6.00	5.75	6.00	5.90	5.55	5.10
Hopper	4.77	5.45	4.95	5.45	5.40	5.15	—	6.00	4.80	5.73	5.93	5.63	5.85	5.60	5.55	5.0
Tube Sheet	4.72	5.40	4.82	5.40	5.35	5.05	—	5.90	4.80	5.55	5.85	5.62	5.75	5.75	5.48	4.9
Weir	4.75	5.40	4.90	5.40	5.35	5.10	4.55	5.90	4.80	5.55	5.85	5.65	5.75	5.75	5.50	4.9

TABLE 2

SUMMARY OF KEY WEST FRACTIONAL FACTORIAL DATA

FREDONIA VALLEY LIMESTONE FIELD TEST DATA (12" ϕ TUBE)

Test Number	F-9	F-30	F-3	F-15	F-16	F-7	F-20	F-10	F-17	F-12	F-21	F-26	F-11	F-29	F-13	F-18
Test Conditions																
Gas Flowrate (scfm)	1468	778	776	1480	798	1475	1453	769	796	1469	1460	770	1497	778	694	1468
Pressure Drop (in. H_2O)	12.0	6.5	6.5	12.0	6.5	12.0	12.0	6.5	12.0	6.5	6.5	12.0	6.5	12.0	12.0	6.5
Stoichiometric Ratio	1:3	1:1	1:1	1:3	1:3	1:1	1:1	1:3	1:1	1:3	1:3	1:1	1:1	1:3	1:3	1:1
Slurry Concentration (wt. %)	5	5	1	1	1	1	5	5	1	1	5	5	5	5	1	1
Particle Size	325	100	325	100	100	325	100	325	100	325	100	325	325	100	325	100
Gas Conditions																
Entering																
Temperature (T_{db})	242	238	223	220	200	239	250	219	200	266	258	210	256	235	214	250
Temperature (T_{wb})	133	132	132	128	125	131	132	130	125	135	133	128	134	132	131	131
SO_2 Concentration (ppm)	414	855	491	775	750	415	830	414	780	414	830	780	414	855	510	840
NO_x Concentration (ppm)	—	—		—					—	—					—	—
Leaving																
Temperature (T_{db})	132	146	146	116	128	126	130	144	131	148	146	136	152	142	138	142
Temperature (T_{wb})	128	129	128	116	113	126	130	126	117	128	128	124	132	126	122	124
SO_2 Concentration (ppm)	58	225	142	135	165	98	420	48	183	106	260	195	207	82	49	435
NO_x Concentration (ppm)	—	—		—					—	—					—	—
Slurry Conditions																
Flowrate (gpm)	1.23	0.40	1.10	10.75	5.75	2.10	0.80	0.60	2.00	6.30	2.30	0.40	0.41	1.20	3.30	4.00
Temperature																
Feed (°F)	78	84	81	67	76	76	80	78	78	80	80	76	80	83	80	78
Effluent (°F)	[illegible]	127	124	114	110	122	117	119	116	124	124	122	125	125	121	123
pH																
Feed	7.68	7.80	7.75	7.75	7.60	7.68	7.60	7.68	7.80	7.70	7.60	7.80	7.70	7.80	7.55	7.80
Effluent	6.13	5.65	4.90	5.47	5.40	5.15	4.75	6.20	4.80	5.80	6.15	4.90	5.20	5.70	5.25	5.40
Hopper	5.99	—	4.98	5.50	5.40	5.12	4.60	6.00	4.77	5.62	5.90	—	4.95	—	5.28	5.05
Tube Sheet	5.92	—	4.88	5.42	5.30	5.00	4.50	5.90	4.70	5.70	5.80	—	4.80	—	5.20	5.00
Weir	5.95	5.55	4.83	5.42	5.30	5.10	4.60	5.92	4.70	5.60	5.80	4.80	4.90	5.60	5.20	5.00

TABLE 3

RESULTS OF SECONDARY REACTANT TEST PROGRAM

Reactant	Gas Flow Rate (SCFM)	Stoichiometric Ratio	Pressure Drop (in H_2O)	SO_2 Removal Efficiency (%)
Lime				
	1445	1:1	6.5	86.4
	790	1:1	12.0	94.9
	782	1:3	6.5	93.4
	1455	1:3	12.0	97.6
Dolomite				
	1430	1:1	6.5	32.6
	1430	1:3	12.0	51.2
	772	1:3	6.5	51.7
	772	1:1	12.0	51.8
Precipitated Calcium Carbonate				
	1431	1:1	6.5	67.4
	778	1:1	12.0	85.5
	773	1:3	6.5	81.9
	1435	1:3	12.0	a

a Sample contaminated due to heavy foaming and carry-over.

NOTE:
1. Slurry concentration - 1% by weight
2. Particle size - no control due to use of commercially available materials.

TABLE 4

SUMMARY OF SHAWNEE NO. 9 FRACTIONAL FACTORIAL DATA

PADUCAH (FVWL) FIELD TEST DATA (8"ϕ TUBE)

Test Number	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16
Test Conditions																
Gas Flowrate (scfm)	442	422	420	426	620	620	617	615	415	415	417	417	617	618	619	619
Pressure Drop (in. H_2O)	6.0	6.0	12.0	12.0	12.0	12.0	6.0	6.0	6.0	6.0	12.0	12.0	6.0	6.0	12.0	12.0
Stoichiometric Ratio	1:1	1:2	1:1	1:2	1:1	1:2	1:1	1:2	1:2	1:1	1:2	1:1	1:1	1:2	1:1	1:2
Slurry Concentration (wt. %)	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Particle Size	325	325	325	325	325	325	325	325	100	100	100	100	100	100	100	100
Gas Conditions																
Entering																
Temperature (T_{db})	180	182	178	156	184	198	197	206	166	188	166	166	204	195	196	196
Temperature (T_{wb})	123	123	122	110	118	116	120	126	118	119	114	114	120	116	116	116
SO_2 Concentration (ppm)	2450	2350	2350	1900	1995	1500	1500	1750	940	940	2200	2200	2230	1450	1470	1470
NO_x Concentration (ppm)																
Leaving																
Temperature (T_{db})	132	132	127	120	113	112	133	138	130	134	129	129	138	131	114	114
Temperature (T_{wb})	110	108	108	101	113	112	113	116	108	110	112	112	116	112	114	114
SO_2 Concentration (ppm)	1175	1080	700	310	765	495	980	1090	440	505	575	660	1420	840	550	475
NO_x Concentration (ppm)																
Slurry Conditions																
Flowrate (gpm)	1.12	2.16	1.08	1.68	1.28	1.94	0.97	2.24	0.81	0.40	1.91	0.95	1.93	1.93	0.94	1.89
Temperature																
Feed (°F)	85	86	86	84	85	86	85	85	88	88	90	90	96	107	98	98
Effluent (°F)	113	110	110	102	114	112	113	116	108	110	112	112	116	112	114	114
pH																
Feed	8.30	8.30	8.30	8.8	8.7	8.7	8.8	8.8	8.4	8.7	8.35	8.35	8.60	8.60	8.60	8.6
Effluent	5.22	5.45	5.10	5.65	5.32	5.45	5.6	5.6	5.75	5.65	5.40	5.25	5.25	5.40	5.35	5.35
Hopper	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Tube Sheet	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Weir	5.20	5.40	5.10	5.60	5.25	5.35	5.5	5.5	5.65	5.55	5.40	5.20	5.20	5.35	5.30	5.30

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TABLE 5

SUMMARY OF SHAWNEE NO. 10 DATA, LIMESTONE INJECTION TEST SERIES

PADUCAH #10 - FV INJECTION FIELD TEST DATA (8" φ TUBE)

Test Number	IP-1	IP-2	IP-3	IP-4	IP-5	IP-6	IP-7	IP-8	IP-9	IP-10	IP-11	IP-12	IP-13
Test Conditions TVA Test No.	8	28	36	29	17	26	27	32	ZTP1	ZTP2	ZTP3	ZTP3	ZTP4
Gas Flowrate (scfm)		525	523	513	522			513	618	618	614	617	368
Pressure Drop (in. H_2O)	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	12.0	12.0	12.0	6.0	6.0
Stoichiometric Ratio	1:1.85	1:3.0	1:0.68	1:1.11	1:2.46	1:1.31	1:1.47	1:1.49	1:0.95	1:0.95	1:1.45	1:0.99	1:0.99
Slurry Concentration (wt. %)	—	—	—	—	—	—	—	—	—	—	—	—	—
Particle Size	400	400	400	400	400	400	400	400	400	400	400	400	400
Gas Conditions													
Entering													
Temperature (T_{db})	198	170	176	207	190	178	204	250	211	211	226	219	200
Temperature (T_{wb})	116	118	118	116	116	114	117	129	122	122	130	130	128
SO_2 Concentration (ppm)	420	760	975	1050	450	495	250	2000	2625	2625	2450	1520	1250
NO_x Concentration (ppm)	—	—	—	—	—	—	—	—	—	—	—	—	—
Leaving													
Temperature (T_{db})	132	126	127	130	128	126	124	138	130	130	131	130	130
Temperature (T_{wb})	110	109	105	112	111	110	105	124	116	116	117	117	117
SO_2 Concentration (ppm)	39.5	46.5	262	285	40	75	30	600	1050	1050	460	540	350
NO_x Concentration (ppm)	—	—	—	—	—	—	—	—	—	—	—	—	—
Slurry Conditions													
Flowrate (gpm)	1.5	1.5	1.50	1.5	1.5	1.5	1.5	1.5	2.0	1.0	2.0	2.0	1.0
Temperature													
Feed (°F)	90	96	102	102	109	100	82	102	98	98	98	102	102
Effluent (°F)	110	108	107	112	111	110	108	124	116	116	117	117	115
pH													
Feed	8.1	8.0	8.0	8.0	8.0	7.8	7.5	8.1	8.1	8.1	8.1	8.1	8.1
Effluent	7.0	6.3	5.4	5.3	6.6	6.0	6.3	5.8	5.2	4.95	6.9	6.4	6.4
Hopper	6.5	6.2	5.3	5.3	6.3	6.0	6.2	5.8	5.2	4.9	6.9	6.3	6.3
Tube Sheet	—	—	—	—	—	—	—	—	—	—	—	—	—
Weir	—	—	—	—	—	—	—	—	—	—	—	—	—

SULFUR DIOXIDE EMISSION CONTROL
FOR
INDUSTRIAL POWER PLANTS

By

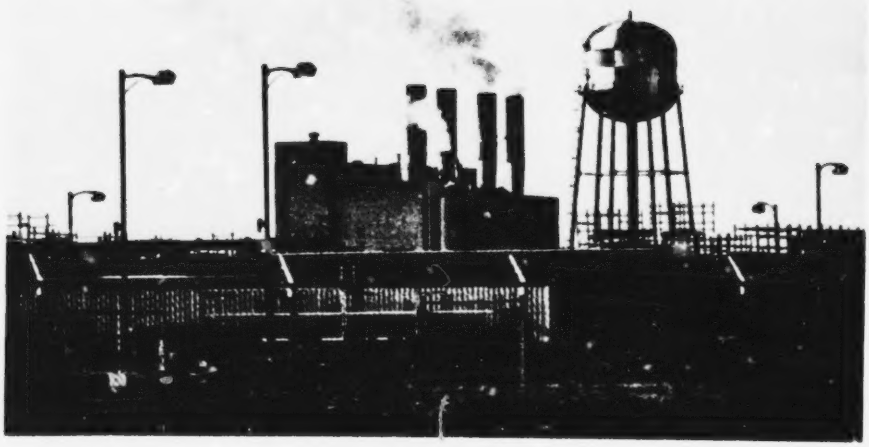
Robert J. Phillips
Project Engineer

GM Manufacturing Development
GM Technical Center
Warren, Michigan

NOVEMBER, 1971

SULFUR DIOXIDE EMISSION CONTROL
BY
WET SCRUBBING

Recent limitations on the emission of sulfur dioxide have forced industrial users of coal to convert to natural gas in order to meet the new codes. This has been necessary because economic means of controlling the emission of sulfur dioxide has not been forthcoming. Many approaches have been offered for the control of SO_2 from large utility boilers, but these approaches are, in almost all cases, based on the recovery of sulfur in some salable form. The small industrial coal user cannot usually justify the expense of such recovery equipment for the small quantity of sulfur involved.



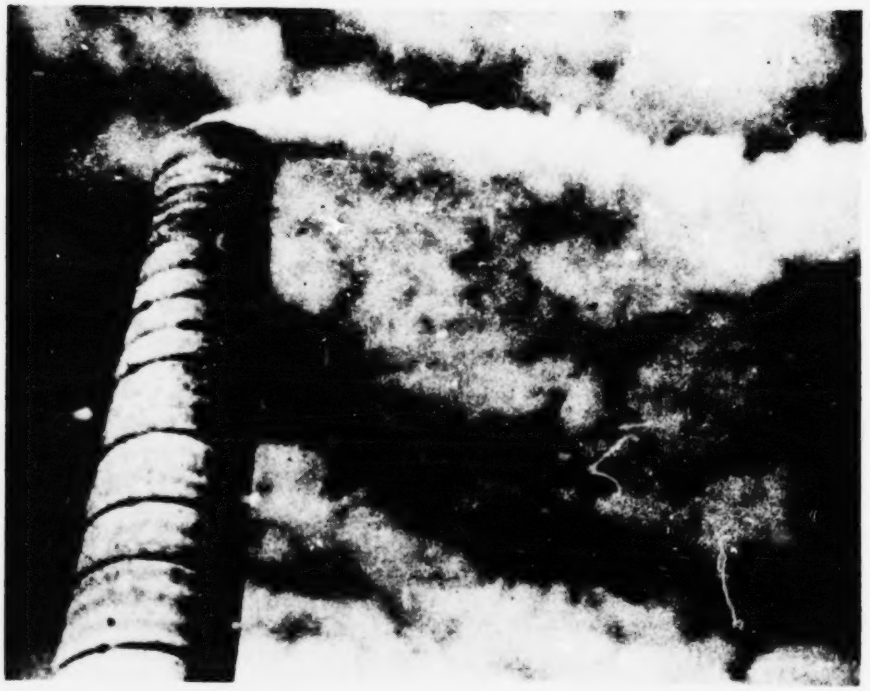
General Motors is a heavy user of coal for industrial powerhouses consuming approximately 2.3 million tons/yr. Because of the long term availability of coal and with the higher cost and deteriorating supply of natural gas, General Motors has made it a policy to continue to use coal wherever economically possible and do it within existing pollution control codes.

Most of the boilers in the corporation range from steaming capacities of 50,000 to 150,000 lb/hr. with an average plant steaming capacity of 250,000 lb/hr.

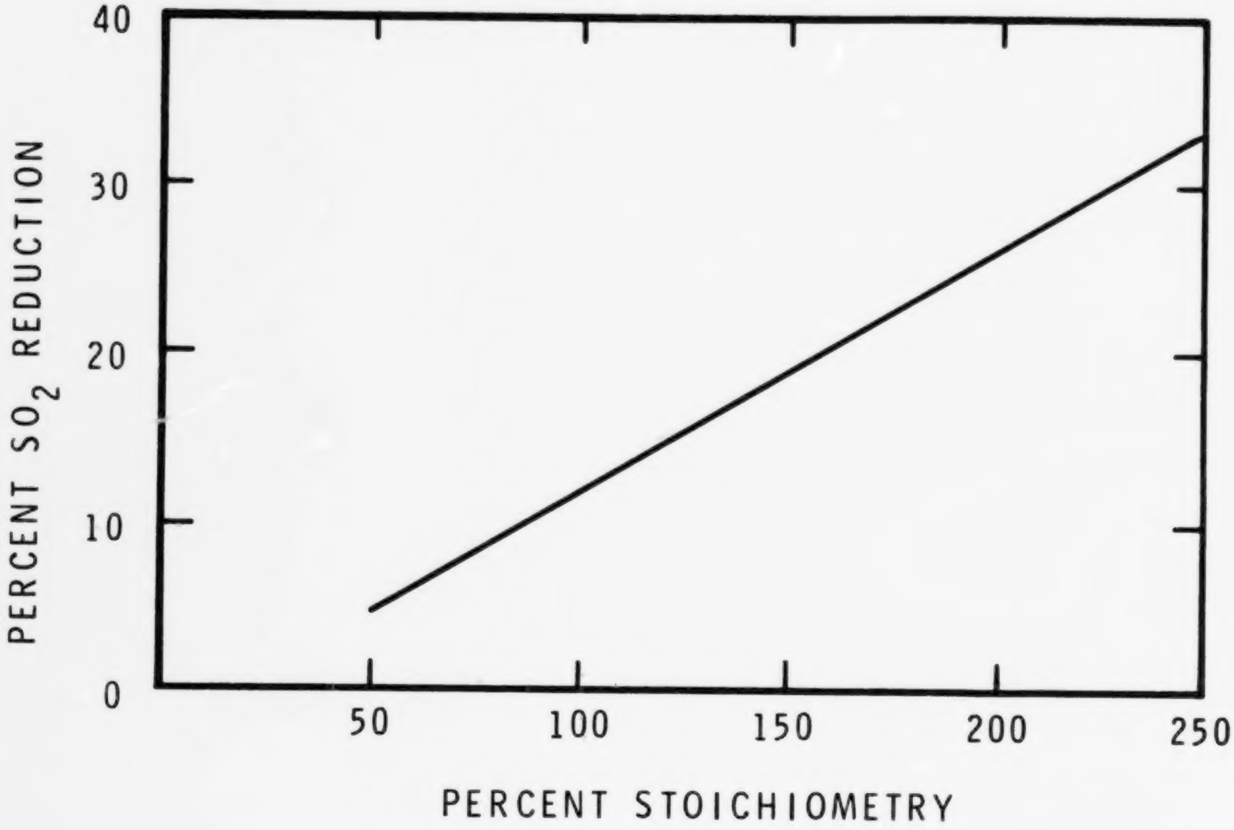
Any SO_2 control process that might be selected had to first meet two corporate criteria.

First - The process must provide an economic incentive over conversion to an alternate sulfur-free fuel.

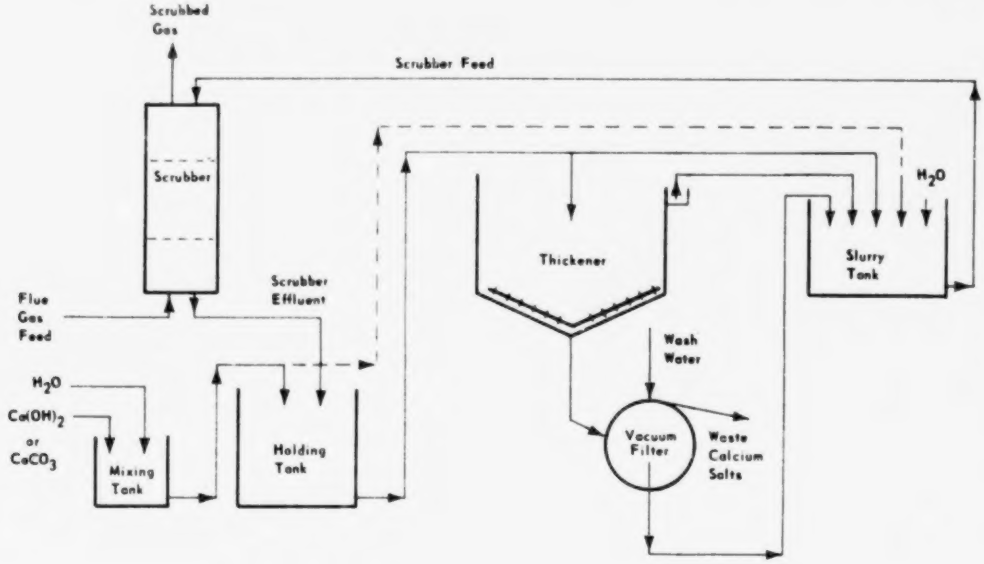
Second- The prime function of the powerhouse is to make steam. The SO_2 control process cannot be so complex as to compete with the steam generating function of the plant. In other words, the SO_2 control process must be nearly control and maintenance free.



We made an evaluation of possible approaches to the control of SO_2. Based on some promising results from tests conducted by the coal industry and subsequent tests run by TVA, it was first decided to try a dry additive injection system to reduce SO_2 emission from our boilers. The dry additive injection system utilizes limestone, dolomite or red mud, either fed in with the coal or injected directly into the boiler. The pulverized stone is calcined in the boiler and reacts with the SO_2 to form a solid calcium sulfate. This sulfate is then collected by the dust collectors.



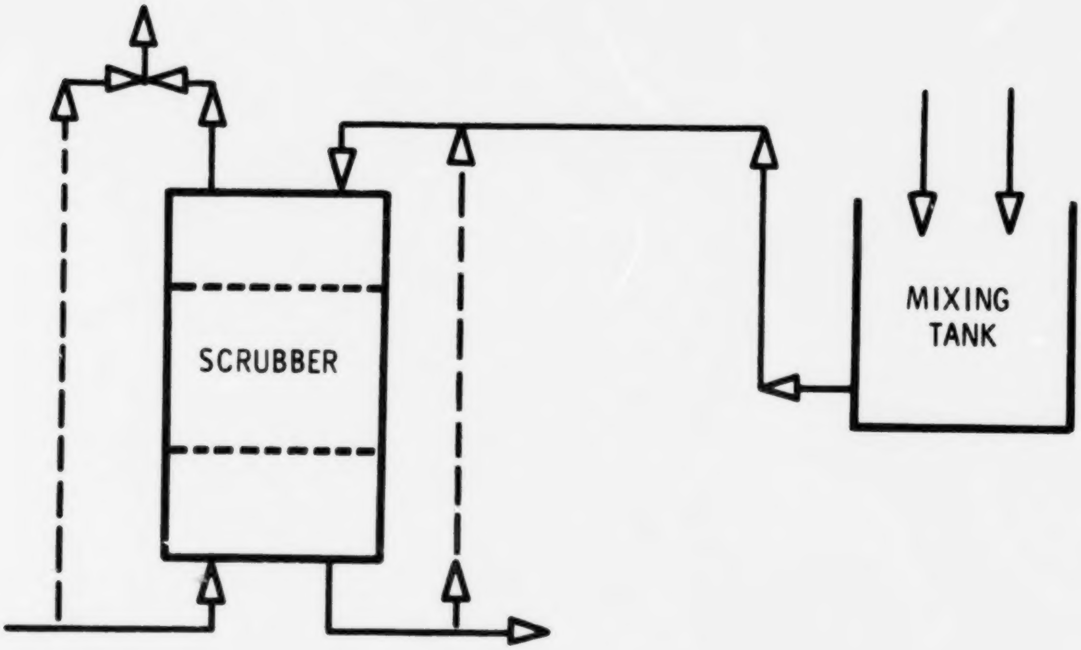
This system presented a very economical approach. Tests were conducted at the Chevrolet-St. Louis powerhouse. These tests showed only a 30% reduction in SO_2 but, at the same time, particulate emissions were increased beyond code limits. Because of the low efficiencies and increased dust loading, it was concluded that the dry additive injection system is inadequate.



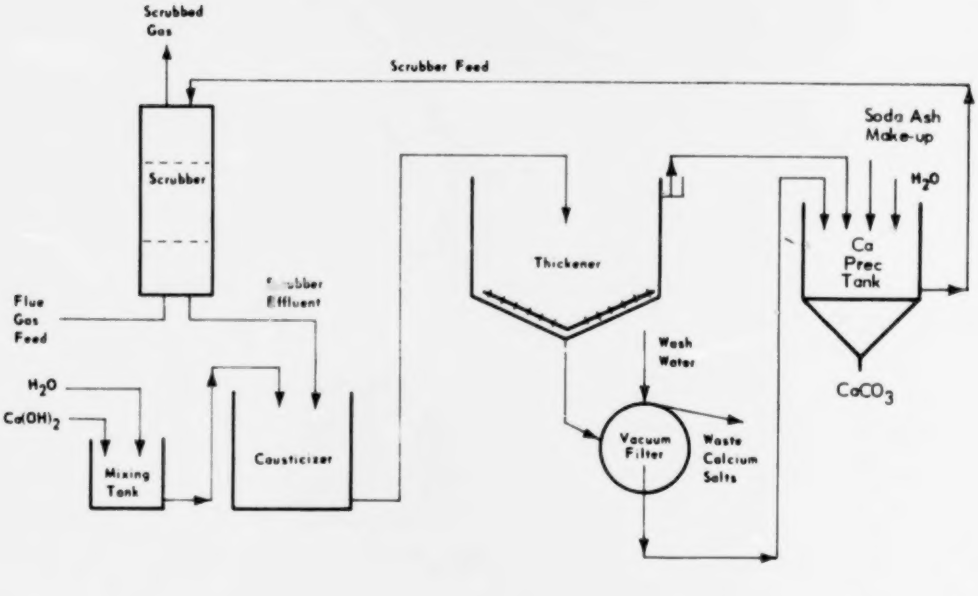
LIME OR LIMESTONE SLURRY SCRUBBING

At the same time as our studies were taking place, other studies involving wet scrubbing of boiler flue gases with lime were also being carried out. The obvious advantage of scrubbing with lime is that $CaSO_3$ is an ideal form for the disposal of the sulfur since it forms an inert solid suitable for land fill. By far the overwhelming problem encountered with the lime scrubber is excessive plugging of the system with insoluble $CaSO_3$. For this reason, we felt that because of the high maintenance required, lime scubbing is not the answer to SO_2 control for industrial size boilers.

SODIUM CARBONATE SCRUBBING



A more practical means of controlling SO_2 can be utilized by substituting soda ash for lime in the scrubber. The obvious advantage of this system is the formation of a soluble product thus eliminating plugging problems. Of course, the formation of a soluble product is an unsuitable form for the sulfur because a water pollution problem has now been created.

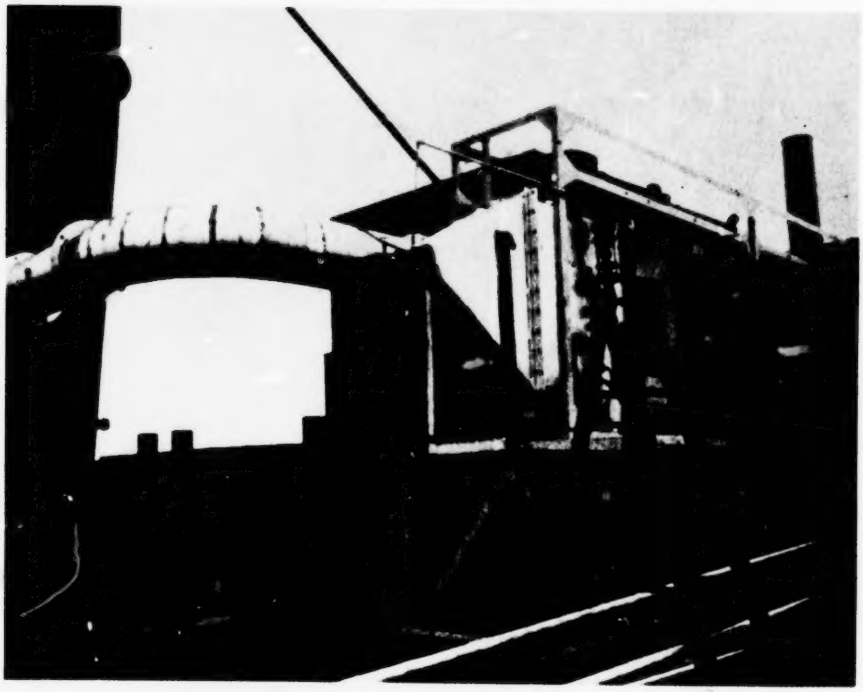


SODIUM HYDROXIDE SCRUBBING WITH LIME REGENERATION

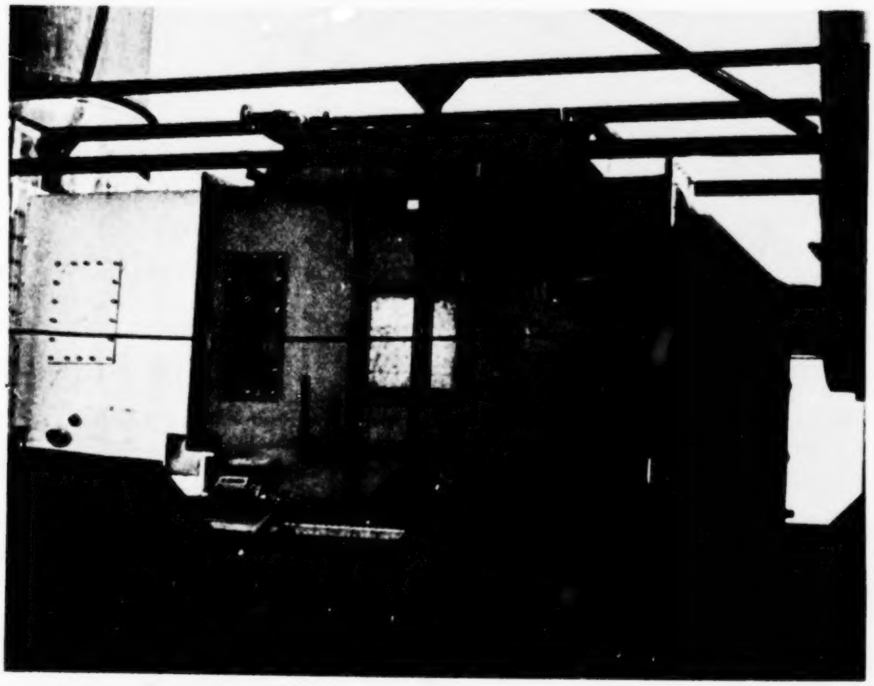
We still felt that wet scrubbing would offer an economic means of controlling SO_2 emissions in industrial boilers. The optimum scrubber system should involve the best parts of both the lime and soda ash system. For this reason, we selected a system using caustic soda for scrubbing with regeneration using lime. In this system a caustic solution is sent through the scrubber. The sodium sulfite formed is then sent to a regeneration tank where lime is added. The sulfur is precipitated from the system in the form of calcium sulfite and sulfate. In the process of precipitating the sulfur, the lime also serves to regenerate the sodium scrubbing solution. In this lime regeneration system, the only product leaving the system is an inert cake.

After some favorable laboratory scale tests, it was decided to run a pilot plant of the system on an actual operating boiler. A critical piece of equipment in the system is the scrubber itself. All of our boilers are equipped with dust collecting equipment so that the scrubber would not have to act as a primary dust collector. Therefore, it was decided that a low energy scrubber would be preferred for the system. Nevertheless, the scrubber would still be exposed to an environment of fly ash and also it must stand up to possible boiler upsets and soot blowing which would increase the fly ash loading a considerable amount for short periods of time. We finally decided that two pilot systems should be run, one utilizing a scrubber that could be classified as a gas absorber for maximum SO_2 removal. The second scrubber was selected for its ability to handle particulates and was considered to be marginal in absorption characteristics.

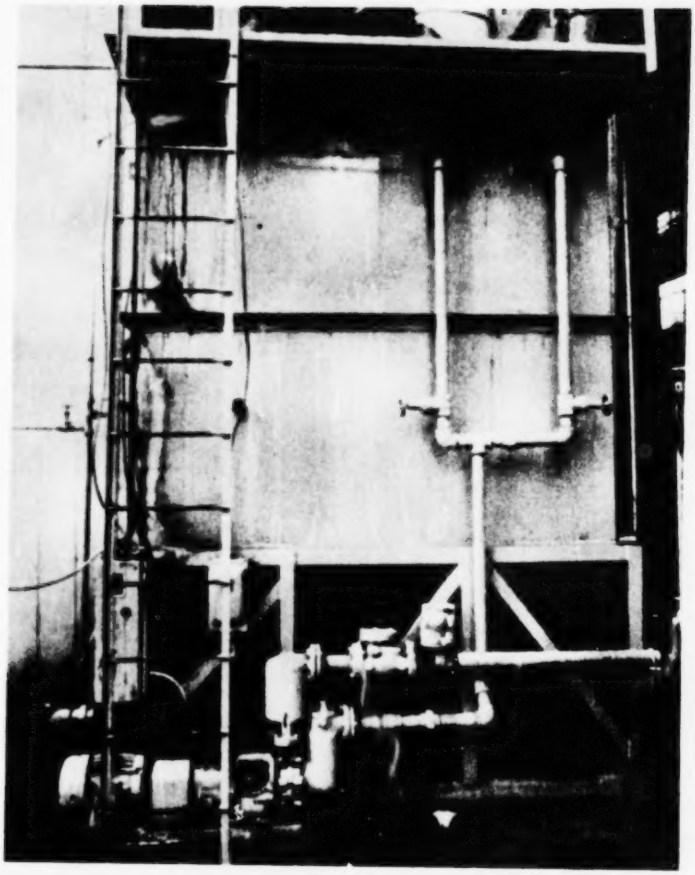
The first pilot system was installed on a powerhouse boiler at Chevrolet-Cleveland. Arrangements were made to use a 2800 cfm packed bed cross flow scrubber for the tests. This scrubber utilizes a plastic packing noted for its good absorption properties. The scrubber contains a packing depth of four feet. 2800 cfm of flue gas (approximately 10% of the total flow) is drawn out of the exhaust stack into a transition piece.



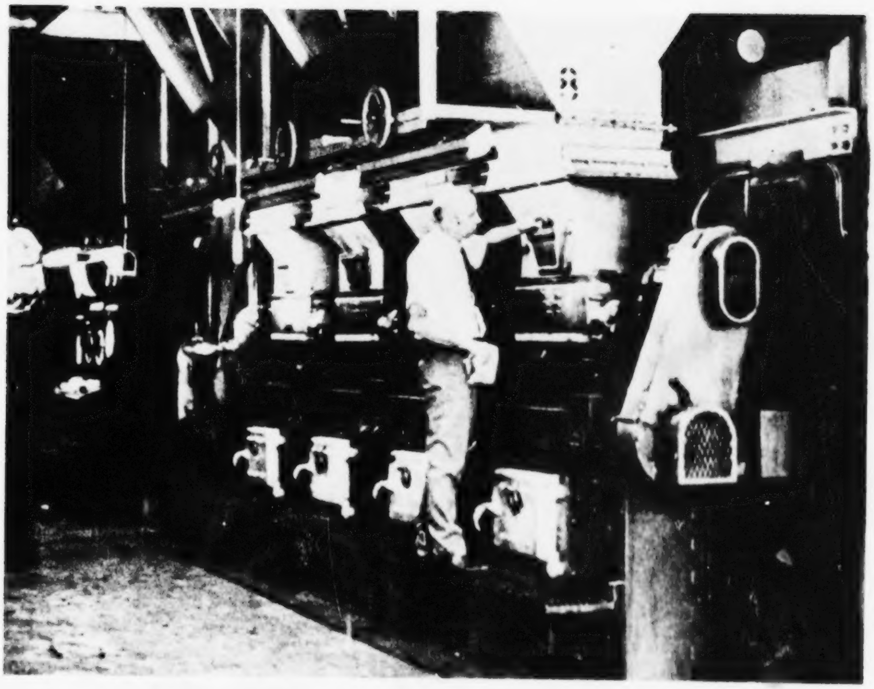
The transition piece was positioned so that it points directly into the gas stream and its diameter was selected so that the gas velocity into the transition duct approximates the stack velocity. This insures that the scrubber is seeing a fairly representative dust loading. The flue gas first enters a quench chamber where the 580° F flue gas is cooled to 130° F by spraying city water thru a series of baffle plates.



The saturated gas then passes horizontally through the four feet of packing. Scrubbing solution is simultaneously being sprayed vertically through the packing. The scrubber is plastic and controls have been installed to insure that the scrubber never sees a high temperature. The caustic scrubbing liquor is sprayed into a series of low pressure full cone nozzles at a rate from 25 to 45 gpm.



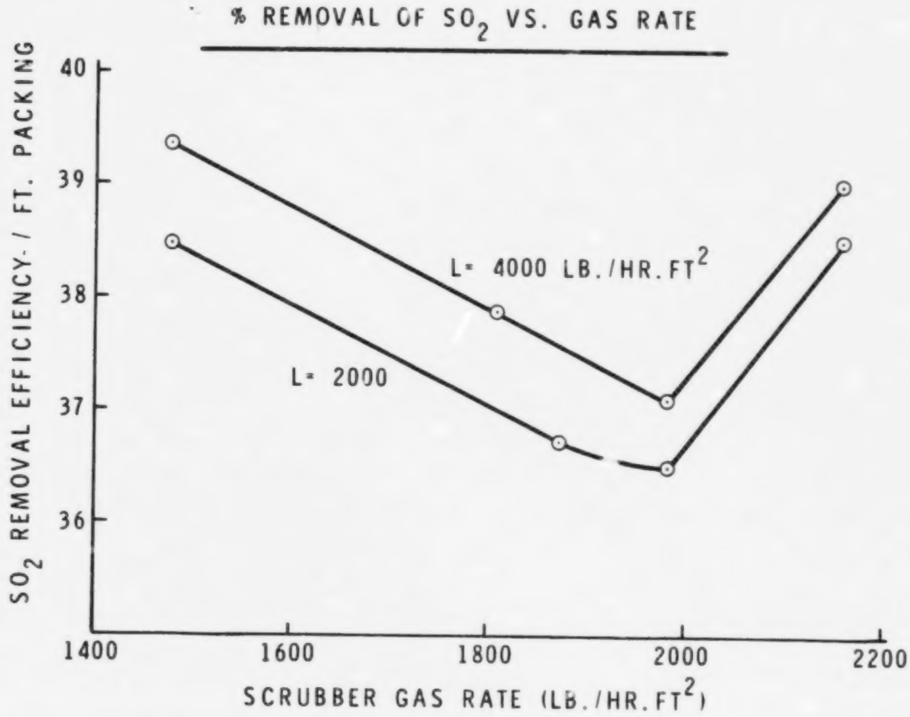
The spent liquor from the scrubber is sent to the regeneration tank which contains both a mixing and a settling section. Lime is added to the mixing section using a lime slurry feeder. The sulfite precipitate is filtered and dried using a vacuum filter. The regenerated liquor is sent back to the scrubber.



The boiler being used for the study is a 80,000 lb/hr. spreader stoker equipped with a multiclone dust collector. A coal with an approximate sulfur content of 2% is used at the plant. The boiler operates with very high excess air (over 100%) resulting in SO_2 scrubber inlet concentrations of about 1000 ppm. The boiler is not equipped with an economizer or air preheater resulting in a flue gas temperature of 580° F.

SO_2 concentrations were monitored using an infra-red analyzer. Test ports were located at both the inlet and outlet of the scrubber. This monitoring capability gave us the chance of changing variables and measuring their effect immediately, thus greatly reduced the time necessary to obtain the needed scrubber design data.

The first tests on the scrubber were run to determine scrubber performance under different operating conditions. The variables with the most affect on scrubber performance were the liquid and gas rates to the scrubber.



In general, the scrubber performance increases as the gas rate is reduced in a scrubber. Our tests have shown that at very high gas rates 2150 lb/hr. ft.^{2}, this characteristic no longer holds. It was found that the scrubber efficiency actually increased from under 37% per foot of packing to 38.5% as the gas rate was increased from 1880 lb/hr. ft.^{2} to 2150 lb/hr. ft.^{2}. It is theorized that at a relatively high gas flow, the increased turbulence that results more than compensates for the reduced contact time in the scrubber.

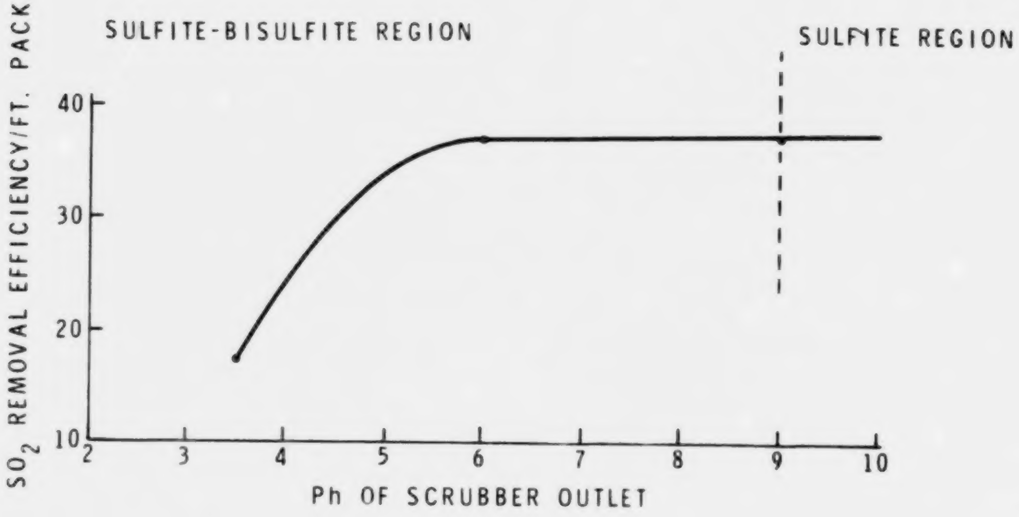
The significance of this result is that high turndown rates on the gas side can be accomplished without loss in scrubber efficiency. This is of considerable advantage for fluctuating boiler loads.

PERCENT SO_2 REMOVAL PER FOOT OF PACKING

LENGTH (FT.)	0	1	2	3	4	5	6	7	8	9	10
SO_2 CONC.	1000	600	360	216	130	78	47	28	16	10	6
% REMOVAL	0	40	64	78	87	92	95	97	98	99	99.4

SINCE THE FORSEEABLE REGULATIONS WILL REQUIRE LESS THAN 90% REMOVAL THE PRELIMINARY ESTIMATE OF LENGTH IS FIVE FEET.

Our conclusions are that the packing efficiency will be approximately 40% / ft. of packing. In the light of forseeable emission regulations, a 90% SO_2 reduction efficiency will be adequate. This will require that a 5 ft. bed of packing be used. It is interesting to observe that if 99% efficiency is required, the length of the scrubber packing must be doubled to obtain this 9% increase.



EFFECT OF CAUSTIC CONCENTRATION ON SO_2 REMOVAL EFFICIENCY

Another factor influencing the scrubber operation is control of caustic in the system. Chemical conversion of the caustic in the scrubber takes place in the following manner:

1st: $NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$
pH 11.5 → pH 9.0

2nd: $Na_2SO_3 + SO_2 + H_2O \rightarrow NaHSO_3$
pH 9.0 → pH 4.0

The reaction can be controlled at any point merely by supplying caustic to maintain a selected scrubber water outlet pH.

As can be seen, there is no loss of scrubbing efficiency until the scrubber outlet pH falls below pH = 6.0, which is greater than 50% into the bisulfite region.

There is considerable advantage in scrubbing into the bisulfite region because of the limitations in producing a high caustic concentration in the regeneration system. If the system operates 50% into the bisulfite region, then the caustic requirements become 1.5 moles NaOH/mole S instead of 2.0 moles NaOH/mole S on a sodium sulfite cycle. This reduction in caustic requirement to the scrubber can be accomplished without loss in scrubber efficiency. The advantage of such operation will become more apparent after a discussion of regeneration chemistry.

Regeneration

Complete regeneration of the spent scrubbing liquor requires that the captured sulfur be precipitated from solution as calcium sulfite and calcium sulfate. These reactions are shown in the following equations:

1) $Na_2SO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_3 \downarrow$

2) $Na_2SO_4 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_4 \downarrow$

It has been found that regeneration of sulfites (equation 1) presents no serious problems. Sulfites are formed by the absorption of SO_2. The relative ease of sulfite regeneration results from the fact that the solubility product (Ksp) of calcium sulfite is very low (6.25×10^{-8} (gm moles)^2 /ℓ^2 @ 115° F). When the product of the dissolved calcium and sulfite ion concentration exceeds the solubility product, calcium sulfite is precipitated.

3) $(Ca^{++}) \times (SO_3^{=}) = 6.25 \times 10^{-8}$

If only sulfites needed to be removed from solution, regeneration would be relatively simple. A portion of the sulfur absorbed in the scrubber appears as sodium sulfate. The percentage of sulfate formation may vary from as low as 10% of the sulfur absorbed to as much as 30% depending on the amount of oxidation that takes place.

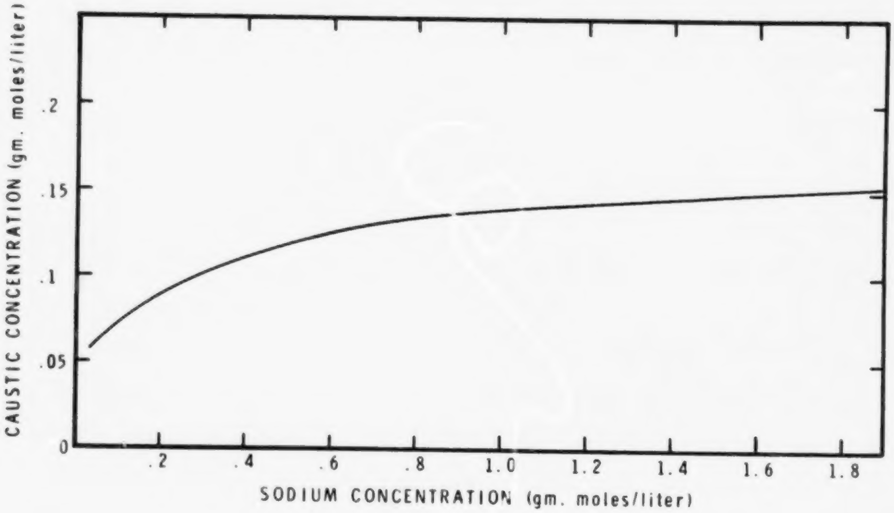
Sulfates do not regenerate as readily as sulfites. The reason for this difficulty is that the solubility product of calcium sulfate is 3.7×10^4 times as great as calcium sulfite. This high calcium sulfate solubility shifts the reaction in favor of sulfate over caustic formation. In order to establish an equilibrium favoring caustic formation, an excess of sulfate ion must be present in solution. This can be done by keeping an excess of sodium sulfate in solution. This excess Na_2SO_4 in solution is necessary for the precipitation of $CaSO_4$ and formation of a dilute caustic solution.

Design of Regeneration System

To effectively operate the regeneration system, there is a minimum sodium requirement needed to precipitate sulfates from the system and form a suitable concentration of caustic. The minimum sodium required to remove a gm mole of sulfur from the system can be summarized as follows:

1) Free sodium (NaOH, $Na_2 CO_3$) required to react with absorbed sulfur (SO_2, SO_3) in scrubber. This includes 2.0 moles Na/mole SO_3 plus,
   a) 2.0 moles Na/mole SO_2 (sulfite cycle).
   b) 1.0 moles Na/mole SO_2 (bisulfite cycle).
2) Sodium sulfate required to reach a favorable solubility product of $CaSO_4$ in solution.

EQUILIBRIUM CAUSTIC FORMATION
IN $Ca(OH)_2$ - Na_2SO_4 SOLUTIONS @ 120°F

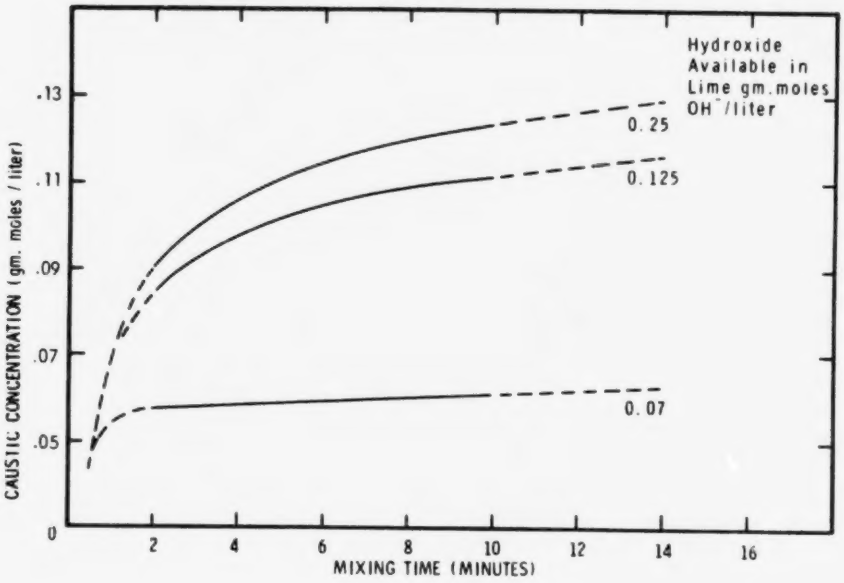


Tests have been conducted to determine the equilibrium caustic formation in sodium sulfate - calcium hydroxide systems. The figure above shows the maximum amount of caustic that can be formed at 120° F in regeneration solutions as a function of sodium concentration. As can be seen, increased Na^+ (indicating increased Na_2SO_4) concentrations decreases the Ca^{++} concentration allowing more OH^- to exist at equilibrium. Beyond 1.0 molar sodium the additional amount of OH^- that can be formed does not increase appreciably.

This equilibrium data shows that no more than a 0.14 molar caustic solution can be produced in 1.0 molar sodium solutions.

The figure does show the limits of caustic that can be formed in the regeneration cycle. It does not indicate the rate of caustic formation which is needed for practical design of the regeneration system.

EFFECT OF LIME AVAILABILITY ON THE RATE OF CAUSTIC FORMATION IN 0.5 MOLAR Na_2SO_4 SOLUTIONS @ 120°F



An additional series of tests were run to determine the rate of caustic formation in 0.5 molar Na_2SO_4 (1.0 M Na^+) solutions.

These tests were run by adding a given amount of calcium hydroxode to 0.5 M Na_2SO_4 solution @ 120° F and drawing samples at 2, 5 and 10 minute mixing intervals. The samples were immediately filtered and titrated with 0.08 N H_2SO_4. In all, three different initial lime concentrations were evaluated.

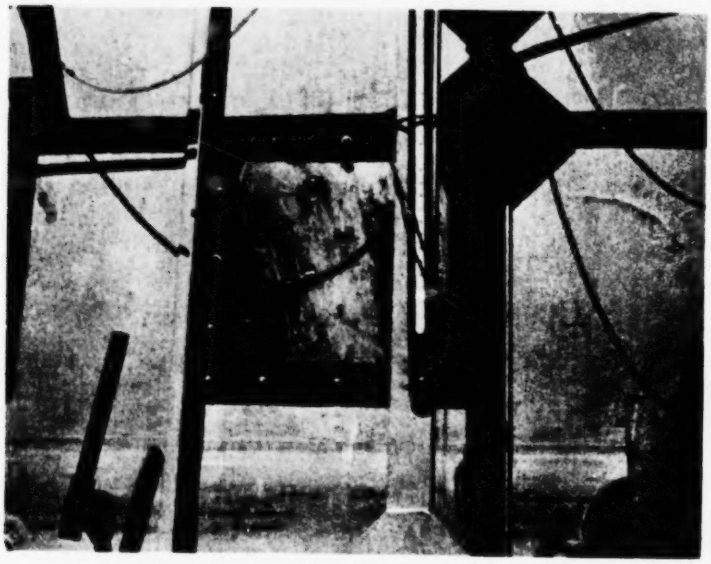
The figure above shows that the rate of lime conversion can be maximized if lime is fed at a concentration near the equilibrium hydroxide concentration (0.14 M). In the 0.125 M OH^- lime feed, 80% conversion of the lime was obtained in 5.0 minutes and 0.1 M OH^- was achieved. When 0.25 M OH^- lime was added, 44% lime utilization was achieved in 5.0 minutes and only 0.11 M OH^- was formed.

These tests concluded that:

1) $Ca(OH)_2$ should be fed at or near the equilibrium caustic concentration of 0.14 gm. moles OH^-/liter.

2) Lime mixing efficiency can be 80% in 5.0 minutes. Recycling of the sludge will have to be evaluated to determine if increased utilization can be obtained.

3) With 5.0 minute mixing, it is felt that 0.1 molar NaOH can be produced for use in scrubbing.



A main advantage of this process is that SO_2 can be removed in the scrubber as a soluble salt. This allows us to use a low energy scrubber for the process. Any calcium carry over from the regeneration cycle will result in deposition in the scrubber. This carry over must be avoided if the process is to retain its advantages over lime slurry scrubbing.

Calcium plugging can occur from two sources -

1st - Carry over of suspended solids.

2nd - Precipitation of dissolved calcium.

Suspended solids can be handled by a gravimetric settling system. A more serious kind of plugging can result from carry over of dissolved calcium into the scrubber. The dissolved calcium is at its solubility product with respect to sulfite and sulfate. Exposure to SO_2 and SO_3 in the scrubber will cause a small amount of precipitation of $CaSO_3$ and $CaSO_4$ in the scrubber if free hydroxide is allowed to enter the scrubber.

We have evaluated one means of eliminating precipitation in the scrubber by using Na_2CO_3 make up as a water softener prior to entry into the scrubber. We were successful in reducing the calcium concentration from 400 ppm to 250 ppm. This, however, will not completely avoid precipitation of sulfites in the scrubber.

Another means of eliminating precipitation in the scrubber would be to operate the scrubber on a low pH loop. The scrubber recycle tank could then be used to precipitate dissolved calcium leaving the recausticizing section. To operate under these conditions, a scrubber with excellent gas absorption characteristics and high liquid to gas flow rates would have to be used. We are now evaluating the possibility of using such a mode of operation.

Pilot Study of Regeneration System

It was found in the pilot plant that production of 0.1 molar NaOH is easily obtainable in 1.0 molar sodium scrubbing solutions at 120° F. During 130 hours of pilot operation no difficulty was encountered in recausticizing the spent scrubber solution. It did become apparent that three variables had a significant influence on the concentration of caustic produced.

1) Mixing time
2) Degree of agitation
3) Rate of lime addition

The mixing section of the solids contact reactor utilized a slow 16 rpm paddle for mixing. It was found that 30 minutes of mixing was required to obtain the desired caustic concentration. It was also found that lime usage was only 70%.

Simulated regeneration tests using near stoichiometric lime addition and high speed flash mixing showed that the lime usage was increased beyond 80%. Also, the mixing time required to produce the same quality caustic was reduced from 30 minutes to 5 minutes.

The amount of lime present in the reaction zone also was shown to have an effect on the concentration of caustic produced as was demonstrated in the laboratory tests. Although higher amounts of lime in the reaction zone produced higher caustic concentration, lower lime utilization was realized.

To further discourage the use of high lime concentrations in the reaction zone, it was found that the spent sludge was chemically inactive even though it contained as much as 30% unreacted lime. Therefore, high lime concentration in the reaction zone would only reduce lime usage because sludge recycle does not appear to improve lime usage.

The final test conclusion was that near stoichiometric lime addition, together with high speed chemical mixing, must be used to optimize lime usage.

Cake Analysis

Na_2SO_4	2.6 %
Na_2CO_3	1.13%
$NaHCO_3$	0.73%
$Al_2(SO_4)_3$	1.84%
$Ca(OH)_2$	0.16%
$CaSO_4.2H_2O$	39.30%
$CaSO_3.2H_2O$	2.93%
$CaCO_3$	4.85%
H_2O	46.5 %

Sludge Settling & Filtering

The $CaSO_3$ - $CaSO_4$ precipitate settled very rapidly. At a clarifier rise rate of 1 gpm/ft.^{2} no turbidity was noticed in the clarified liquid. The thickened sludge contained 20% solids which was taken to 50% solids in the rotary drum vacuum filter.

An analysis of the filter cake was made. This analysis gives only an indication of the content of the cake and cannot be considered representative.

A considerable period of time elapsed before the cake was analyzed. The degree of sulfite oxidation and carbonation cannot be determined. The high amount of gypsum does indicate that high oxidation takes place in the scrubber. There is no explanation for the high $Al_2(SO_4)_3$ content in the filter cake. Silicon was also identified in significant quantities in the sample indicating that aluminum may be present in the form of aluminum silicate rather than sulfate.

This cake analysis also indicates better than 80% lime usage where system material balances indicated only 60 to 70% usage.

An evaluation of the settling of the precipitated $CaCO_3$ in the softener was not made in the pilot plant. Instead, an in-line filter was used to remove the precipitated $CaCO_3$.

Livonia Scrubber

Concurrent with these tests being conducted, another scrubber is being tested at the Chevrolet-Livonia powerhouse. This unit is a wet cyclone scrubber. It is primarily known for its ability to handle particulate matter. The unit has the same capacity as the packed scrubber unit and operates with a multiple stage impingement wash of the flue gas. The pilot scrubber we are using contains four stages with a capacity for two additional stages.

The scrubber is located on the exhaust of a 80,000 lb/hr. spreader stoker equipped with a multiclone collector. The boiler has an economizer so the scrubber inlet temperature is about 350° F.

The gas is cooled and saturated in the first scrubbing stage rather than using a pre-quench as in the packed scrubber. There is also no regeneration cycle in this system since it was decided that all necessary information for regeneration could be gained with the packed scrubber. We mainly are interested in seeing whether this scrubber, with marginal gas absorption characteristics, is capable of removing sufficient amounts of SO_2.

Sulfur dioxide removal tests were run on the 4 stage scrubber. Results showed an 87% SO_2 removal efficiency. This efficiency was higher than expected. The scrubber pressure drop was 5.0" H_2O during the tests. An additional two scrubbing stages is now being installed and the scrubber will be re-tested. It is hoped that the additional two stages will bring the overall SO_2 removal efficiency above 90%.

BENEFITS

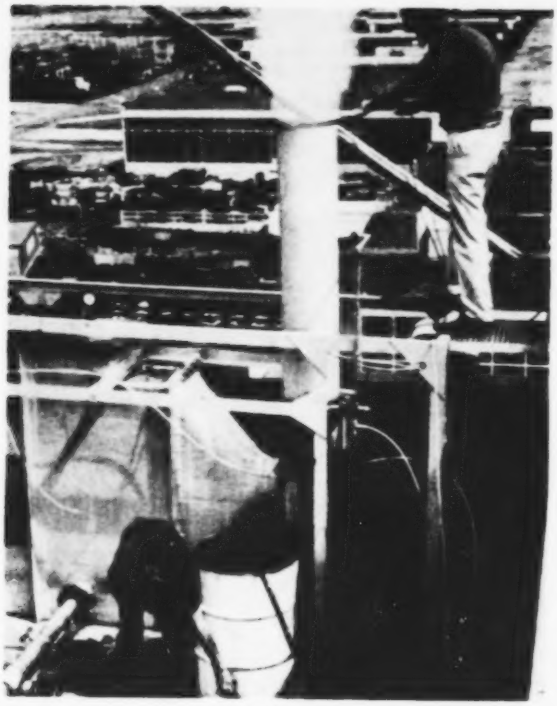
1. Greater than 90% sulfur dioixde removal efficiency.
2. Low energy scrubber (3" - 7" H_2O)
3. Soluble scrubber (no plugging)
4. Inert by-product
5. Economically feasible

It is our conclusion that the caustic-lime regeneration system presents a practical means for control of SO_2. Efficiencies in excess of 90% are easily obtained with standard low energy scrubbing equipment. The scrubber is not in danger of plugging as in a lime system because the lime is restricted to the regeneration tank. The sulfite cake formed can be readily disposed as sanitary land fill.

PROCESS ECONOMICS

Installed Capital Costs	\$ 3.20/lb. steam/hr.
Operating Costs	\$ 3-4/ton of coal

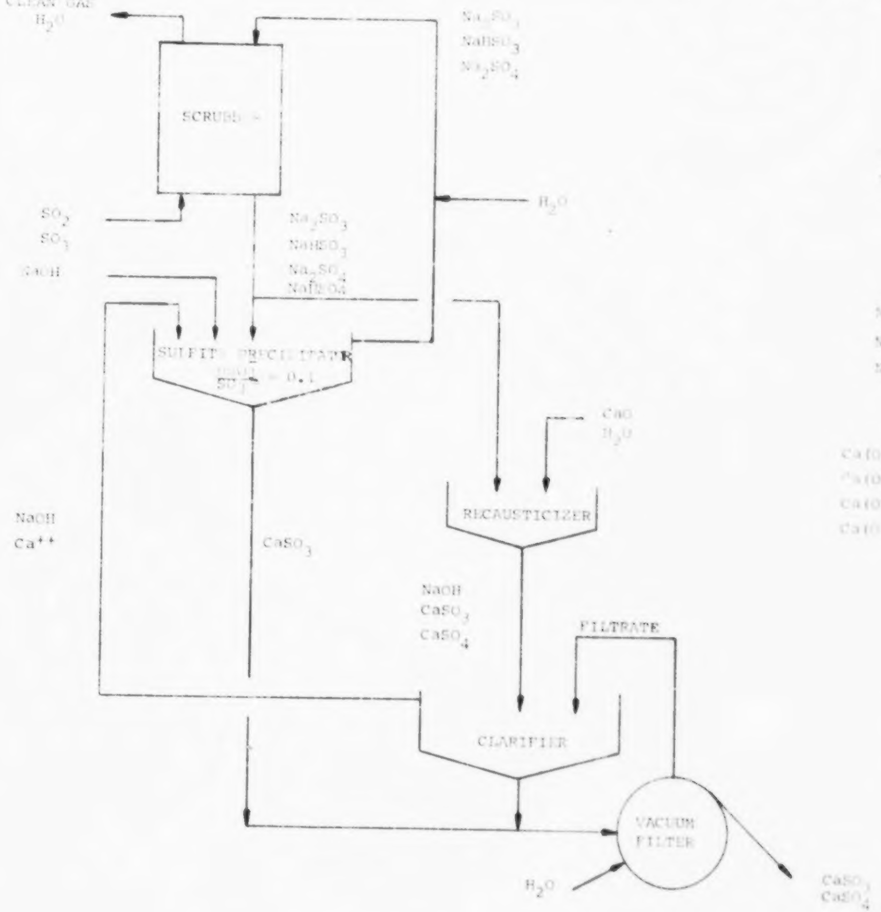
An economic evaluation of SO_2 control methods was made. The results indicate that the caustic-lime regeneration shows favorably over other possible alternatives. Fixed capital costs for the system are estimated at about \$3.20/lb. steam. Operating costs will be approximately \$3.00 - \$4.00/ton of coal.



Another benefit of the system is that particulate emissions now below code in the 0.2 - 0.3 grains/scf range will be reduced by 70% +.

In our tests we have found no appreciable formation of nitrite or nitrate ion in water analysis. We have concluded that oxides of nitrogen are not being absorbed in the system.

To sum up -- the conclusions from our work are that we do have a workable and economic process for the control of sulfur dioxide emissions from coal burned in industrial sized power plants. This should be of considerable benefit to many industries in the very near future, and it certainly will be of great benefit to our environment.



SCRUBBER CHEMISTRY

$SO_2 + H_2O \rightleftharpoons H_2SO_3$

$SO_3 + H_2O \rightarrow H_2SO_4$

$Na_2SO_3 + H_2SO_3 \rightleftharpoons 2NaHSO_3$

$Na_2SO_4 + H_2SO_4 \rightleftharpoons 2NaHSO_4$

$2NaHSO_3 + O_2 \rightarrow 2NaHSO_4$

SULFITE PRECIPITATOR CHEMISTRY

$NaHSO_3 + NaOH \rightarrow Na_2SO_3 + H_2O$

$NaHSO_4 + NaOH \rightarrow Na_2SO_4 + H_2O$

$Na_2SO_3 + Ca^{++} \rightarrow CaSO_3\downarrow + 2Na^+$

RECAUSTICIZER CHEMISTRY

$Ca(OH)_2 + NaHSO_3 \rightleftharpoons NaOH + CaSO_3\downarrow + H_2O$

$Ca(OH)_2 + Na_2SO_3 \rightleftharpoons 2NaOH + CaSO_3\downarrow$

$Ca(OH)_2 + NaHSO_4 \rightleftharpoons NaOH + CaSO_4\downarrow + H_2O$

$Ca(OH)_2 + Na_2SO_4 \rightleftharpoons 2NaOH + CaSO_4\downarrow$

MANUFACTURING DEVELOPMENT
Manufacturing Staff
General Motors Corporation
Warren, Michigan

Title:

PROCESS FLOW SHEET

G.M. Double Alkali SO_2 Scrubbing Process

SULFUR OXIDE CONTROL AT THE COPPER SMELTER

by

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and

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SECOND INTERNATIONAL LIME/LIMESTONE WET SCRUBBING SYMPOSIUM
New Orleans, November 8-12, 1971

SULFUR OXIDE CONTROL AT THE COPPER SMELTER

Although the basic chemistry of the principal reactions in various sulfur dioxide control processes is the same regardless of the source of sulfur dioxide, conditions prevailing at the copper smelter relevant to sulfur dioxide removal processes differ in several significant respects from those prevailing at other industrial sources of sulfur dioxide.

This paper reviews the state of the art of sulfur dioxide control as applicable to the copper smelter and the Smelter Control Research Association's pilot-plant program. Some of you may not be familiar with the Smelter Control Research Association. The Association was founded and incorporated as a nonprofit association by the eight primary copper producers of this country for the specific purpose of developing processes for removal of sulfur oxides and particulates from smelter stack gases and more especially for conducting pilot-scale investigation of the removal of sulfur dioxides from reverberatory furnace off-gases. The reasons for emphasizing the reverberatory gases will be discussed later.

The eight founding companies of the Smelter Control Research Association are: American Smelting and Refining Company, The Anaconda Company, Cities Service Company, Copper Range Company, Inspiration Consolidated Copper Company, Kennecott Copper Corporation, Newmont Mining Corporation, and Phelps Dodge Corporation. These companies account for all of the primary copper smelter production in the United States.

Results of the Association's experimental programs will be published and will be available to the public. It should be emphasized that the programs of the Association supplement extensive in-house development work being conducted by the individual copper companies.

As background for our discussion of sulfur dioxide control as applied to copper smelters, it will be helpful to first describe, in general terms, a typical copper smelter operation and to note the operations in which sulfur dioxide is generated and the conditions under which it is formed.

To simplify the description reference will be made principally to the flow of the copper-bearing materials and of the sulfur.

Most copper ores today are much too low in copper content to be processed directly. Therefore, it is necessary to separate the copper-bearing minerals from other materials in the ore in which they occur. After crushing and grinding of the ore, the copper-bearing minerals are concentrated by a flotation process. The composition of the concentrate varies from smelter to smelter, but the copper content is usually in the range of 10 to 30 % and the concentrate contains, on an average, a pound of sulfur or more for each pound of copper since it is produced from sulfide ores. The concentrate also contains a number of trace constituents, some of which are known to affect certain of the sulfur dioxide control processes, particularly those involving the use of catalysts.

Smelters throughout the world rely on oxidation processes to remove the sulfur and this oxidation generates sulfur oxides. A typical smelter produces approximately two pounds of sulfur dioxide for each pound of copper, since a pound of sulfur forms two pounds of sulfur dioxide.

Foreign smelters employ flash, electric, and blast furnaces, as well as reverberatory furnaces; but our domestic practice, which has been keyed to the available raw materials, is based on the use of reverberatories. At some smelters, the concentrate goes through a roasting operation before being fed to the reverberatory furnace. The roasters, typically fluid bed reactors, generate a relatively uniform, concentrated stream of sulfur dioxide, i.e., 10-15 % sulfur dioxide. In most cases, the concentrate is fed directly to the reverberatory furnace where it is fused in an oxidizing atmosphere, forming a slag and a molten mixture of copper and iron sulfides known as matte. Approximately one-third of the sulfur in the concentrate is eliminated at the reverberatory furnace as gaseous sulfur dioxide which is discharged to the stacks. The matte is discharged from the reverberatory furnace into ladles in which it is transported to converters. In the converters, the matte undergoes further oxidation, additional slag is formed, and the balance of sulfur is discharged as sulfur dioxide. The converter product is approximately 97 to 98 % pure, and is known as blister copper. The blister copper is further refined to produce the high purity product required for industrial applications.

The reverberatory furnaces are large, rectangular, refractory chambers, usually in excess of 100 feet long and 30 feet wide. They are fired with gas, oil or coal. The reverberatory furnace off-gases contain, on an average, around 1 % sulfur dioxide, along with a variety of trace constituents as noted earlier. The gases, on leaving the furnace, are usually in excess of 2000°F, but a feed stream from a typical fluesystem would probably be on the order of 400-500°F.

The converters are cylindrical, refractory-lined vessels, usually 30 feet long and 13 feet in diameter, although a few larger units are now in use. The operation of the converter is cyclic, and the concentration of the sulfur dioxide in the exhaust gases varies widely during the operation. The average sulfur dioxide content of the exhaust gases during the blowing operation is usually in the range of 4 to 6 %. This variability in sulfur dioxide concentration is a definite handicap in the sulfur dioxide control process. Smelters operating sulfuric acid plants try to program their converter operation, coordinating the cycles of converters in order to provide a more uniform flow of sulfur dioxide to the acid plant. This objective is difficult to attain and is a significant constraint on the smelter operations and does not, in any event, produce a highly uniform flow to the acid plant.

It will be seen, then, that two distinct levels of sulfur dioxide concentration occur at the copper smelter. The converters and roasters produce off-gases relatively concentrated in sulfur dioxide, averaging, in the case of the converters, around 4 - 6 % sulfur dioxide. The reverberatory furnace produces a much more dilute gas, ranging from a fraction of 1 % to somewhat in excess of 1 % sulfur dioxide.

Technology is commercially available for converting the sulfur dioxide in the more concentrated streams, i.e., from the converters and roasters, to sulfuric acid. Seven acid plants are in operation in the copper industry today, and additional plants are either under construction or in the planning stage. There is, however, no commercially proved technology available for the removal of sulfur dioxide from the more dilute gases produced in the reverberatory furnace.

The Smelter Control Research Association program is, accordingly, directed as noted earlier, specifically to the development of processes for removal of sulfur dioxide from reverberatory furnace off-gases.

It should be noted that although reverberatory gases are more dilute than converter gases, they are on an average at least 3 to 5 times as concentrated in sulfur dioxide as typical utility stack gases. In the wet-lime and wet-limestone scrubbing processes, this higher concentration represents a significant difference, particularly with respect to control of scale formation in the scrubbing system.

It is fortunate that there are strong similarities in the problems involved in removal of sulfur dioxide at the three concentration levels we have referred to, i.e., the 0.1 to 0.3 % and lower level prevailing generally at utility and industrial boilers, the 1 % level at the reverberatory furnaces, and the 4 to 6 % and higher levels found at the converter and the roaster. However, sulfur dioxide removal systems for each application present distinct and separate problems. Verification of any process under consideration must, therefore, be carried out under conditions valid for the proposed application. Therefore, pilot-scale tests on actual smelter gas are considered essential before the very substantial commitment that would inevitably be involved can be made to a given control process. For this reason the Association's pilot-plant tests, as we noted earlier, are to be conducted on actual lter gas.

In establishing priority to be assigned to investigation of various possible alternatives for removal of sulfur dioxide from low-strength gases at the smelter, the stringent time schedule being imposed on the industry for sulfur oxide control dictated that priority be assigned to alternatives deemed closest to commercial availability, even though other alternatives might provide a more satisfactory long-range solution.

The time schedule and the economic facts of life dictated that the control system be compatible with existing facilities, i.e., that the system be what is commonly referred to as an "add on" system. After reviewing more than 100 processes or variations of processes, the Smelter Control Research Association selected wet-limestone scrubbing for its initial pilot-plant study on the basis that this process, which has been investigated extensively by the Environmental Protection Agency and by the utility industry, was closest to commercial availability.

A pilot plant has been constructed and is in operation at the McGill, Nevada smelter of the Kennecott Copper Corporation. The pilot plant is rated at 4000 SCFM and is of sufficient size to permit extrapolation to full commercial scale. (The extrapolation would be approximately 20 to 1.)

The pilot plant has been designed with a view to optimum versatility and will be used in testing wet-lime and sodium sulfite scrubbing as well as limestone scrubbing. In addition, lime regeneration of the scrubbing liquid in the sodium sulfite system is to be evaluated. The tests on the sodium sulfite system will, hopefully, with information available from other operations on sulfur dioxide desorption permit evaluation of the sodium sulfite absorption-desorption process vis-a-vis the throw-away process.

The plant employs a Turbulent Contact Absorber in series with a venturi. Limestone-water slurry flows countercurrent to the gas stream from the Turbulent-Contact Absorber to the venturi. A bleed stream from the venturi is sent to a centrifuge where the reaction products are separated and discharged, the liquid being returned to make-up tanks for recycle. Operation with lime will be essentially the same as with limestone.

When sodium sulfite is used as the absorption medium, the bleed stream from the venturi will be sent to causticizing tanks where calcium sulfite will be precipitated on addition of lime. The product will then be sent to the centrifuge for separation of the calcium sulfite which will be discharged as a slurry, as in the limestone scrubbing system. The liquid from the centrifuge will be returned to a holding tank where make-up caustic will be added to provide a fluid suitable for recycling.

The pilot plant has been in operation with limestone approximately two months, on a 24-hour per day, 5-day per week basis. In initial operation, the scrubbing liquid was not recycled. Once-through operation was employed to minimize plugging of equipment with reaction products. This was done to facilitate operations while the operators were familiarizing themselves with the system. The plant is now a closed-loop operation.

It is too early to present any final conclusions with respect to the effectiveness of the system in smelter gas control. Results to date may be summarized as follows:

The average sulfur dioxide recoveries have been approximately 70 per cent from 0.7 per cent sulfur dioxide streams and approximately 55 per cent from 1.0 per cent streams.

A high calcium limestone has been used in all tests. Bench-scale tests of a number of high calcium limestones indicated that the limestones tested were equally reactive. Bench-scale tests of additional limestones are planned.

Limestone usage has been varied from 1.2 times stoichiometric to 2.0 times stoichiometric.

Both 90% minus 200 mesh stone and 95% minus 325 mesh stone have been used in the pilot plant. Any difference in the reaction rates with the two grinds is apparently masked by other process variables. Although one might anticipate increased reactivity with the finer grind, no significant improvement in sulfur dioxide recoveries has been noted to date with the use of the finer grind.

The sulfur dioxide recoveries do appear to decrease as the concentration of the sulfur dioxide as the feed stream increases.

In this regard, it should be noted that the concentrations of sulfur dioxide in the feed stream varies and extended runs are required in order to obtain meaningful data. Over shorter periods variations in the gas concentration may mask the effect of other variables.

Our current efforts are directed to establishing the factors controlling sulfur dioxide removal efficiencies in order to optimize sulfur dioxide recovery. Development of techniques for effective control of scale formation is also a major objective.

We would like to emphasize again that there are significant differences in the problems involved in sulfur dioxide control at the smelters and at other industrial sources of sulfur dioxide.

The gas flows are generally lower than at the utilities. A typical commercial unit on a reverberatory furnace would handle approximately 80,000 SCFM.

The sulfur dioxide concentration of reverberatory gas is much higher, averaging around 10,000 ppm, i.e., 1%, and is much less uniform than that of industrial boilers.

The total dust loading at the smelter is lower than that at many utility boilers because of the lower gas volumes, but the concentration is somewhat higher than at typical coal-fired boilers. Trace constituents of the smelter gas stream will not only be different than at the utilities but will vary from smelter to smelter. These constituents may have little or no effect on some control processes but are known to affect others, and their possible effect must be determined in actual pilot-plant tests.

The percentage of oxygen in reverberatory gas streams is highly variable, and is normally higher than that in exhaust gases from utility boilers.

The gas flow from the converter is cyclic. While the gas flow from the reverberatory is much more uniform, it, too, is subject to variation.

From the standpoint of disposal of waste products, the smelters have, in most cases, for the moment at least, available sites to establish sludge ponds, and this is not as serious a problem as it would be in more heavily populated areas. However, the problems involved in handling the very substantial quantities of raw materials consumed in the control process operation and the tonnage of waste products that must be disposed of do present a substantial materials handling problem.

While the situations at the smelter, with respect to disposal of the throw-away product, may be more favorable than that at the utilities, the situation with respect to disposal of potentially marketable products such as sulfuric acid and sulfur is much the reverse, since the smelters, in many cases, are remote from potential markets.

As noted earlier, the Smelter Control Research Association supplements extensive in-house developments by the individual Member Companies. A few of these may be briefly mentioned:

1. A 1,000 SCFM ammonia scrubbing plant was operated for about eight months at a copper smelter to determine whether the process, which had been in successful operation for a number of years at a lead-zinc smelter was, in fact, adaptable to copper reverberatory gas.

   The sulfur dioxide recovery achieved in the pilot plant was in accord with recoveries from available theoretical data as well as from prior practice. The problems encountered were: (1) aggravated corrosion; (2) high sensitivity to irregular draft conditions; (3) a stack discharge of highly visible particulate matter which required additional collection devices; and (4) requirements for high volumes of low temperature water, an extremely important consideration in many smelter locations. Perhaps the most compelling factor, however, is that the operation of a full-scale plant would produce large quantities of soluble ammonium compounds which would create disposal and pollution problems of their own unless they had utility as usable or salable products.

2. A 400 SCFM pilot plant utilizing sodium citrate as the absorbent for sulfur dioxide was operated for about six months at another copper smelter. The process calls for the sulfur dioxide loaded absorbent solution to be treated with hydrogen sulfide to form elemental sulfur, part of which would be reacted with methane to make up the hydrogen sulfide requirement. The pilot operation, which included only the absorption and regeneration steps, was beset with mechanical problems, and solution losses were incurred which prevented reliable evaluation of citrate consumption, an obviously important parameter. Recovery of sulfur dioxide from the reverberatory gas stream ranged between 90 and 99 per cent. The hydrogen sulfide generation step in the process was not investigated.

3. Another copper smelter is currently installing an industrially sized operating module to explore the commercial feasibility of absorbing the sulfur dioxide in reverberatory gas with dimethylanaline (DMA), and springing the sulfur dioxide in highly concentrated form to feed an acid plant, or perhaps a sulfur plant. DMA absorption has been successfully demonstrated

in small lead smelter applications treating gases above 3.5 per cent sulfur dioxide. The unit under construction will be treating a much leaner gas and is expected to be on-line by mid-1972.

4. A $1.7 million sulfur reduction pilot plant designed to produce 8 to 20 tons of elemental sulfur per day has been recently placed in operation as a joint venture of two copper smelting companies. Its main objective will be to perfect a suitable process for reacting sulfur dioxide with reformed natural gas to form elemental sulfur. The pilot plant will operate on gases ranging from 12 to 100 per cent sulfur dioxide.
5. A number of smelters have conducted bench-scale tests or even operated small pilot plants to explore the potential of absorbing sulfur dioxide in naturally occurring or industrially produced materials readily available to them. Such waste products as fly ash concentrate tailing pulps, furnace slags, and others have been tried. In general, the sulfur dioxide loading capacity of these sorbents is not high, and their usage would require prohibitatively large tonnages unless they were effectively regenerated, and this step has not been successfully demonstrated.

In addition to their work in the five areas mentioned, individual smelters have been exploring, in pilot plants already completed or being planned, changes in the smelting process itself by which pollution abatement may be furthered. This test work relates particularly to the development of methods of continuous smelting, which would greatly enhance the efficiency of appurtenant sulfur recovery processes.

In addition, the potential of electric smelting is being explored by several companies and a 7500 KVA electric furnace is presently being installed at a large chemical plant with a small copper smelting annex.

It is evident that the copper smelting companies are on the move in their efforts to control sulfur oxide emissions.

PROTOTYPE AND FULL SCALE TESTS

H.W. Elder, Chairman

Participants:

James Jonakin and James Martin
B.G. McKinney and A.F. Little
M. Epstein, F. Princiotta, R.M. Sherwin, L. Szeibert, I.A. Raben
R.M. Sherwin, I.A. Raben, and P.P. Anas
J.D. McKenna and R.S. Atkins
Gerhard Hausberg
J.J. O'Donnell and A.G. Sliger
Tsukumo Uno, Masumi Atsukawa, and Kenzo Muramatsu
Lyman K. Mundth
J.H. McCarthy and J.J. Roosen
Robert R. Padron and Kenneth C. O'Brien
J.A. Noer and A.E. Swanson
J.W. James
D.T. McPhee
J.F. McLaughlin, Jr.
D.C. Gifford
H.P. Willett and I.S. Shah

PROTOTYPE AND FULL SCALE TESTS
(PARTS I, II, AND III)

Second International Lime/Limestone Wet Scrubbing Symposium
New Orleans, Louisiana
November 8-12, 1971

H.W. Elder, Chairman

SUMMARY

The increasing interest in preserving a quality environment in this country and abroad has caused an accelerating movement toward enactment of legislation to limit discharge of undesirable materials to the atmosphere. The existing and pending laws have started a somewhat frantic search for methods to control emission of materials classified as pollutants. The participants and attendees at the Second International Lime/Limestone Wet Scrubbing Symposium assembled for a critical analysis of one of the more promising methods for removal of SO_2 from stack gases.

The session of the symposium on prototype and full-scale application of the process covered topics from plans for full-scale installations to availability of raw materials. The main theme that evolved as the session progressed was the concern over reliability of the scrubber system as compared with the power plant. The problem of waste disposal was a popular subject and, as might be expected, economics was a controversial issue.

Participants in the prototype and full-scale session are listed below.

Name	Company
Masumi Atsukawa	Mitsubishi Heavy Industries, Ltd.
A. O. Blatter	Union Electric Company
D. C. Gifford	Commonwealth Edison Company
J. W. James	Ontario Hydro
Jim Jonakin	Combustion Engineering, Inc.
Ulrich Kleeberg	Gottfried Bischoff KG
L. K. Mundth	Arizona Public Service
J. H. McCarthy	The Detroit Edison Company
J. D. McKenna	Cottrell Environmental Systems
B. G. McKinney	Tennessee Valley Authority
D. T. McPhee	Kansas City Power and Light
J. A. Noer	Northern States Power Company
J. J. O'Donnell	M. W. Kellogg Company
R. R. Padron	Key West Utility
F. T. Princiotta	Environmental Protection Agency
R. M. Sherwin	Bechtel Corporation
H. P. Willett	Chemical Construction Corporation

Use of lime or limestone scrubbing for control of SO_2 emission in stack gas is of interest because it is relatively simple compared with processes that produce salable products, both fly ash and SO_2 may be removed, limestone is available in most parts of the country, earlier work has shown the process is feasible, and the complexities of marketing sulfur products are avoided. A better understanding is needed of factors that influence chemical scaling, solids deposits, slurry settling rates or mechanical dewatering, erosion, and mist carryover.

Limestone can be added to the system in two ways--either addition in the boiler where the carbonate is decomposed or addition directly into the scrubber circuit. The calcined material is more reactive and should result in a lower raw material requirement. However, there is evidence that scaling is more likely to occur during closed-loop operation with lime than with limestone. Also, occurrence of calcium-containing deposits in the convection pass was reported for operation during limestone injection. It is likely that relatively wide tube spacing would be required to prevent plugging. The risk of tube fouling could be avoided by addition of calcined lime directly in the scrubber, but the cost of lime is high and the scaling tendencies are a deterrent. However, the process apparently has been developed successfully in Japan and a 20-mw prototype unit is being installed on an oil-fired boiler.

The major interest appears to be in use of limestone in the scrubber. Plans for equipping over 3000 mw with tail end processes were discussed. The plants range in size from 37-580 mw and scheduled startups vary from January 1972 to May 1977. It was interesting to note that all stressed the importance of reliability and many have included scrubber bypass systems, redundant installed equipment, and modular construction. Methods of solids disposal varied from use of only settling ponds to barge transport of slurry to a remote location followed by mechanical dewatering and return of the clarified liquor. The concensus was that waste disposal is likely to be a major cost item. Stabilization of sludge by the addition of fly ash was reported. Materials of construction varied but in all cases the scrubbers are lined with polyester glass or rubber.

One presentation dealt mainly with a fairly detailed cost analysis for a tail end system. The capital requirement for a 180-mw retrofit unit amounted to \$49/kw and the operating cost was estimated at about \$4/ton of coal. Others reported estimated capital costs ranging from about \$20-\$60/kw.

In spite of the increasing commitment to full-scale application of the lime/limestone scrubbing processes many questions remain unanswered. The EPA-funded, prototype-scale demonstration of the process at TVA's Shawnee Steam Plant is designed to fully characterize the process with limestone added in the scrubber circuit, calcined lime added in the scrubber, and limestone injected into the boiler followed by wet scrubbing.

The system was designed by Bechtel Corporation. Three parallel scrubbers each designed to handle 30,000 acfm of gas will be operated simultaneously with closed-loop operation. Each train is equipped with a thickener and the underflow from a single unit can be further dewatered in a centrifuge or filter. A separate settling pond is provided for the test facility.

The test program will begin with a break-in phase to establish system integrity followed by statistically designed screening experiments to identify the effects of variables and will be concluded by long-term operation at optimum conditions to verify reliability. The system is extremely flexible and well instrumented to obtain maximum information.

It was reported that limestone is available in most parts of the country in quantities that are sufficient for the installed generating capacity. Moreover, because of the abundant reserves, the price is likely to be relatively stable for the foreseeable future.

APPLICATIONS OF THE C-E
AIR POLLUTION CONTROL SYSTEMS

by

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Presented at

SECOND INTERNATIONAL LIME/LIMESTONE WET SCRUBBING SYMPOSIUM

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Sheraton-Charles Hotel, New Orleans, Louisiana

APPLICATIONS OF THE C-E
AIR POLLUTION CONTROL SYSTEM

James Jonakin

James Martin

Much has been said in the technical press on the subject of air pollution from power plant boilers and the C-E systems for meeting this problem. A brief review will serve to introduce the full-scale commercial activities C-E has been engaged in.

Requirements for electric power in the U. S. will increase from 1.5 trillion kwh in 1970 to over 3 trillion kwh by 1980. To meet this demand for power, generation capacity must increase from the present 340 million kilowatts to about 710 million kilowatts and all available fuel sources - nuclear, coal, oil, and others - must be used. By 1980, nuclear energy is expected to supply about 21% of the total installed capacity while a substantial portion of the remaining capacity will be supplied by coal. In the face of this continuing demand for electric energy from fossil fuels, utilities and equipment manufacturers must work toward decreasing pollution while at the same time keeping the cost of the end product, electricity, at a reasonable level.

POLLUTION EMISSIONS

As coal is burned in the furnace of a steam generating unit, a number of combustion products are formed, of which 98.7% are non-pollutants. The primary concern of the power industry is particulate matter, sulfur oxides, and nitrogen oxides. Particulate matter accounts for 80% of the polluting effluent, while sulfur oxides and nitrogen oxides make up the remaining 20%. These three pollutants represent only 1.3% of the total stack effluent, a rather small portion but a very significant quantity.

When all combustion processes in the U. S. are taken into account and the figures are based on yearly emissions of pollutants into the atmosphere, then the total is of concern, as shown in table 1. These quantities will increase in proportion to the amounts of fossil fuel consumed unless additional control methods are developed and applied. Pollution from carbon monoxide and hydrocarbons are almost two-thirds the total; however, their source is primarily from automobiles, trucks, airplanes, etc. and will not be discussed in this presentation. Note that the tons of particulate matter emitted is the smallest of the totals listed. Although a "heavy" potential polluter accounting for 80% of the polluting effluent from a steam generator, present technology is generally adequate to reduce emission of particulate matter to the level shown. Electrostatic precipitators are available with a removal efficiency of better than 95%.

CONTROL OF SULFUR OXIDES

The control of sulfur oxides emissions, however, presents some difficult problems. Trace quantities of sulfur oxides have to be removed from millions of cubic feet of gas on a continuing basis. As an example, over 2 million ft^3 of gas is discharged from the stack of a 700,000 kw steam generating unit each minute. The gas resulting from the combustion of a coal containing 3% sulfur contains only 0.2% sulfur oxide.

Sulfur oxides can be controlled by two general methods:

1. by burning low sulfur fuels which occur naturally, or are produced by removing the sulfur from the fuels before combustion, or

2. by removing sulfur oxides from flue gases after combustion.

Natural gas contains no sulfur, but the supply of this fuel in the U. S. is limited and the proven resources are shrinking rapidly. The use of this premium fuel by utilities is decreasing and cannot be considered a general solution to the pollution problem.

Fuel oil produced from crude oils originating in North Africa and the Far East contains less than 1% sulfur and many utilities on our east coast are now burning this fuel. However, drilling and tanker capacities are somewhat limited and its cost has increased as the demand has increased. In addition, the rapidly changing political situation in these countries jeopardizes this source of oil. The high sulfur Central America and Middle East oils are more economical and the supply is more stable.

The coal used by electric utilities in the USA contains an average of 2.2% sulfur but ranges from <1% to >5%. In the eastern and midwestern states where about 80% of the total power is produced, most coals contain >3% S. There are large supplies of low sulfur coal in the Western U. S., but for the most part, it is located far from major population centers or market centers, therefore, it has not been mined commercially on a very large scale.

STACK GAS CLEANUP

Of the two methods of controlling SOx emissions, the present emphasis of industry is on stack gas cleanup rather than removing sulfur from the fuel before combustion. There are numerous schemes for removal of SO_2 and particulate matter from stack gases. They have been described in some detail in various publications.

Wet scrubbing has received the most attention because of its low cost and simplicity. Combustion Engineering is offering two wet scrubbing systems: "furnace injection" and "tail-end". These systems can be termed "throw away" systems since the process is not dependent on the recovery of a salable chemical by-product.

SULFUR RECOVERY AND WASTE DISPOSAL

The descriptive term "throw away" implies indiscriminate rejection of by-products, and carries the stigma of conversion of one form of pollution to another. C-E is not blind to this situation and continues to investigate all aspects of the problem.

A cost comparison of the C-E wet scrubbing process vs sulfur recovery processes is shown in table 2. In the U. S., therefore, the present systems for stack gas cleanup must be used at least as an interim measure. At the same time C-E has established research programs for the investigation of by-product utilization and waste disposal. This subject is covered in another C-E paper at the conference, entitled, "Research and Development in Wet Scrubber Systems".

FURNACE INJECTION SYSTEM

The furnace injection process involves injecting an additive which contains a large percentage of calcium or magnesium, such as limestone or dolomite, into the furnace of a steam generating unit. The schematic arrangement has been shown in many papers. Here, the additive is calcined, producing a more reactive compound which then chemically reacts in the dry state with some of the SO_2 and SO_3 in the combustion gases to form compounds of calcium and magnesium. About 20 to 30 percent of the sulfur oxides, including all of the SO_3, is removed in the dry state.

Next, the flue gas containing unreacted SO_2 and calcined additive flows to the wet scrubber, a large tank-like structure containing water sprays and a bed containing glass spheres. In the scrubber, the remaining calcined additive chemically reacts with the water and the remaining SO_2. At the same time, the fly ash is scrubbed from the gas. The solution containing the compounds formed by these reactions and fly ash drains out the bottom of the scrubber to a clarifier or pond where the solids settle. Clarified water is then available for recirculation. The cleansed flue gas passes through a mist eliminator for removal of moisture and then is reheated for fan protection and reduction of stack plume.

The development of C-E's air pollution control system started in 1964 with the construction of a small pilot facility in our laboratories. This was followed by a second pilot application on a unit at the Detroit Edison Company in 1966 and 1967.

APCS CONTRACTS - FURNACE INJECTION SYSTEM

1. Union Electric - Meramec No. 2 - 140 MW

2. Kansas Power and Light - Lawrence No. 4 - 125 MW

Installation of the APCS systems for these two existing units was completed in late 1968. Operation of these demonstration units has revealed problems, and modifications have been made to the scrubbers, water control piping, and the additive injection procedure. Our Research and Product Development Department has been actively involved in the solutions to these problems, which are described in detail in their paper on wet scrubber systems. Data obtained to date show that SO_2 emission when burning coal with 3.5% sulfur has been reduced to the equivalent of burning a 1% sulfur coal, and that at least 99% of the particulate matter is removed.

These units are pictured in Figures 1 and 2 respectively.

3. Kansas Power and Light - Lawrence No. 5 - 420 MW

The contract for this unit, obtained in 1968, is for a new C-E boiler. This unit is just starting up and has fired natural gas during startup. Coal will be fired beginning about mid-November 1971 and the APCS will be tested.

This unit is pictured in Figure 3.

4. Kansas City Power and Light - Hawthorne No. 3 - 100 MW

5. Kansas City Power and Light - Hawthorne No. 4 - 100 MW

The contracts for these two units were obtained in 1970. They are presently being installed and are scheduled for operation next year.

TAIL-END SYSTEM

The other C-E air pollution control system, designated "tail-end", is similar to the furnace injection method except a slurry of pulverized limestone or slaked lime is used to scrub the flue gases. No furnace injection of additive is required. Results obtained in prototype units show that 80% or more of the SO_2 can be removed with a particulate matter removal efficiency of 99% or better.

The schematic arrangement for the contracts with this system is approximately similar to that for the KDL prototype unit, shown in the paper on wet scrubber systems. The system is designed for a variety of situations in which furnace injection can be eliminated. Some of these situations are:

a. Providing flexibility in the selection of the most suitable additives.

b. Supplementing existing electrostatic precipitators on older units.

c. Replacing precipitators for the removal of particulates as well as SO_2, as in the case of one contract described below.

APCS CONTRACTS - TAIL END SYSTEM

6. Louisville Gas and Electric - Paddy's Run No. 6 - 70 MW

The contract for this unit, an existing boiler built by a competitor, was obtained in 1970. Of interest is the fact that this contract will use carbide sludge, a waste material, as the additive for reducing SO_2 emissions. The utility will obtain the carbide sludge from a local industrial firm which has large quantities of this waste product produced in the manufacture of acetylene. In other words, a "throw away" product from another industry is recycled to improve the environment.

To ensure that the carbide sludge would be an adequate additive, tests were conducted in our new laboratory prototype unit. This 12,500 cfm unit, the largest laboratory test unit of its kind, has been running almost constantly since its startup in early 1970. A tremendous amount of research data has been collected which has helped us in adapting systems to the specific requirements of customers. Most important, however, it has helped us to accelerate progress in the development of a commercially operable APCS.

7. Union Electric - Meramec No. 1 - 125 MW

This contract was obtained in 1971. The boiler is a duplicate of Meramec No. 2, for which a furnace injection system was supplied, in item 1 above.

8. Northern States Power - Sherburne No. 1 - 700 MW

This contract, also obtained in 1971, is significant for two reasons:

a. It is the largest contract so far, for either of the two C-E systems. The boiler is a 1970 contract, a C-E controlled circulation unit burning a sub-bituminous coal.

b. The coal has a sulfur content of less than 1% and experience has shown that this fact is detrimental to the efficiency of electrostatic precipitators. It is for this reason that the wet scrubber system was selected and the primary object is particulate removal, although about half the sulfur in the fuel will be removed by the scrubbers. This system and the reason for its selection will be described in a paper to be given by Mr. Noer.

APCS CONTRACTS - FIELD EXPERIENCE

The initial operation of the air pollution control system has previously been discussed. Subsequent operation has revealed additional problems and also has allowed C-E to further refine the modifications made to the original APCS design. The following is a summary of the modifications made to system components.

Sootblowers

The installation of half-track sootblowers on the scrubber inlet in 1969 has eliminated the problem of massive inlet deposits. These sootblowers have been in service at Union Electric Meramec #2 and Kansas Power and Light Company Lawrence #4 for over 7000 hours of coal operation. Only one serious buildup of deposits has occurred during that time. The oscillating motor on one of the inlet blowers failed and was not discovered immediately. In approximately 24 hours a large deposit developed, which had to be removed manually.

The sootblowers have been operating at normal blowing pressures and have not required any abnormal maintenance. All future C-E - APCS are being supplied with inlet sootblowers similar to those on the existing units.

Ladder Vanes

The installation of ladder vanes on the units at KP&L Co., Lawrence #4 and U.E. Co., Meramec #2 helped solve the problem of gas distribution in the scrubber but in the final analysis could not successfully be kept clean. The ladder vanes were removed in 1970.

Further work has been done at our Kreisinger Development Laboratory to determine if a less complicated system of ladder vanes can be used to improve the scrubber's gas distribution but not provide such a large surface for deposition. In addition, more sophisticated wash systems are being designed.

Spray Piping

Deposition on the underbed spray piping has been reduced dramatically by the use of strategically placed wash nozzles and the installation of some quenching nozzles at the inlets of the scrubbers.

The use of some synthetic materials to prevent corrosion has led C-E to the conclusion that the material best suited to the environment of the scrubber is fiberglass. Piping, either made from fiberglass or coated with fiberglass hasbeen installed in the existing field units. In addition, the use of fiberglass coatings on other scrubber surfaces has been tried successfully.

Nozzles

Underbed spray nozzle pluggage is another problem we have encountered. Deposit formation in the bed area is directly related to proper operation of spray nozzles and distribution of spray water. Nozzle plugging with bits of scale and miscellaneous debris which happen to enter the spray water system as well as a need for proper mixing of spray water and recycle slurry water led to the development of a special nonclogging nozzle. There have been no serious pluggage problems in the field units since installation of the nozzle. Both overbed and underbed recycle of slurries have been accomplished with these nozzles.

Bed Plugging

Bed plugging of two types has been experienced at both existing demonstration units. They are defined as follows:

1. Deposits formed by mechanical means. Deposits formed because of low gas velocities in sections of the scrubber bed fall in this category. These deposits may be cementitious in nature because of the mixture of solids found in the scrubber, but usually can be washed away with a fire hose.

2. Deposits formed as a result of precipitation of a slightly soluble calcium salt such as calcium sulfate, calcium sulfite, or calcium carbonate. The scales formed by these deposits are always crystalline in nature and are usually very difficult to remove.

The control of these two types of bed pluggage has been accomplished by the use of higher liquid to gas ratios, to prevent mechanical deposits, the addition of extra make-up water to the system to dilute the concentrations of the slightly soluble calcium sulfate, and the implementation of closer controls on the system's chemistry to prevent calcium sulfite and carbonate scale.

Work in our research laboratory is just being completed which is expected to eliminate the use of the extra make-up water for calcium sulfate scale control.

Mist Eliminators

The mist eliminators above the marble bed became coated with deposits during early runs. The throughput gas velocity was raised, and consequently, the dewatering capability was greatly reduced. The demisters were cleaned, and a wash system was installed above the demister section to be operated off-line, as required. Deposition on the demister vanes has been reduced during operation under steady conditions at moderate loads.

Laboratory studies were undertaken in 1971 to develop an improved mist eliminator which could sustain higher gas velocities than present designs and also lend itself to washing better than the existing demister.

Water table studies suggested that a two stage L-shaped demister would be more satisfactory than the present Z-shaped demister. Air-water models were constructed in our laboratory at Windsor, Connecticut. The evaluation showed that the double L-shaped demister would have considerably more throughput capacity than the existing design and that it could be washed much more easily. This two stage L-shaped demister is presently being installed at Kansas Power and Light Company on both units and has been incorporated on all future APCS.

Reheaters

The reheaters have been "plastered" with deposits a number of times during previous operation. The improvement in scrubber bed gas distribution and the installation of half-track sootblowers have made it possible to maintain the gas side pressure drop across the reheater. Operating experience has led to the conclusion that, in the damp atmosphere above the demisters, a steel-on-steel construction was necessary to provide fin strength to withstand blowing pressures required for clean operation. The initial reheaters were replaced with an arrangement of the heavy duty finned tubes to allow for efficient cleaning by scheduled sootblower operation.

Our experience during the last twelve months since the redesigned reheaters were installed has revealed that the present reheater design coupled with half-track sootblowers are adequate if the demister is performing as designed.

On two or three occasions during the last year, improper demister operation has caused excessive reheater deposition at both Kansas Power and Light Company, Lawrence #4 and Union Electric Company, Meramec #2. The new demister design previously described should eliminate this problem.

Drain Line Scale

During June, 1969, operation of the APCS at Union Electric, a calcium sulfite scale was found in scrubber drain line to the clarifier. It was theorized that some of the calcium oxide entering the scrubber was falling out in the scrubber bottom. This CaO would then begin to hydrate as it was conveyed down the scrubber drain line to the clarifier. This hydration would cause a rise in the pH of the scrubber effluent. Since the scrubber effluent contains a high concentration of calcium bisulfite, an upward shift in pH would cause a conversion of calcium bisulfite to sulfite and a shift in solubility and probably produce the observed calcium sulfite scale.

To eliminate this problem, the bed overflow pots were tied off and piped to the clarifier separately thereby insuring no shift in solubility. The calcium oxide that fell out in the scrubber bottom was conveyed to a well-mixed recycle tank and then pumped up above the scrubber bed in order to utilize this additive.

This system has undergone extensive testing at both Union Electric and Kansas Power and Light Company. It has been determined that the calcium oxide cannot be injected in the bed without calcium sulfite scale occurring. A modification to the recycle system was made at KP&L Company in the spring of 1971. A portion of the pot effluent slurry was pumped to the recycle tank and thoroughly mixed with the calcium hydroxide slurry. It was determined that if the proper amount of pot effluent slurry was used (i.e., utilized to control the recycle tank pH essentially) no scale was produced when the material was recycled and yet significant improvement in sulfur dioxide absorption could be achieved. This improvement ranged from 200-400 ppm additional sulfur dioxide removal depending on the stoichiometric amount of limestone being fed.

Furnace Operation

Kansas Power and Light Company has been able to operate the APCS for periods of four weeks or longer at a time without serious plugging developing in the back-pass of the boiler. Additional sootblowers have been ordered but have not been installed to date.

Union Electric Company Meramec #2 has experienced back-pass plugging which has required high pressure cleaning. The economizer of this unit is extremely close spaced and is normally difficult to clean. In addition, the tubular air heater does not lend itself to the furnace injection APCS as well as the regenerative air heater. The application of the furnace injection system to existing units requires a thorough evaluation of the back-pass of the boiler to prevent problems similar to those experienced at Meramec #2.

Other Field Work

During 1970 the application of wet-scrubbing for particulate removal from boilers fired with low sulfur and low ash coal was evaluated at the Naughton Station of Utah Power and Light. A scrubber having one marble bed and two marble beds in series, and a rod type scrubber were tested. Results indicate a particulate reduction to 0.02-0.035 grains per Standard Cubic Foot (SCF) of dry gas for the marble bed and rod type scrubbers operated at a 6-10 inch pressure drop. Increasing the pressure drop across the rod type scrubber resulted in a reduction of the particulate matter below 0.01 grains per SCF of dry gas.

Field testing was continued at Meramec Station #2 of Union Electric Company and Lawrence Station #4 of Kansas Power and Light Company to evaluate a new nozzle design, variations in recycle methods and limestone addition on the removal of SO_2 and deposit formation on the scrubber components. SO_2 removal up to 70 percent was achieved. Interrupted operation due to change to gas firing to meet load demands did not permit completion of scheduled testing program at Lawrence. (This unit is capable of operation at higher loads on gas than coal.)

Following equipment revisions to incorporate new knowledge and experience test programs were undertaken at both field units in 1971 in the following general categories:

1. Operation without recycle

2. Operation with overbed recycle
3. Operation with underbed recycle
4. Simultaneous operation of both underbed and overbed recycle

Results were:

Kansas Power and Light Lawrence #4

The test program on recycle optimization was completed. Tests were run with above and below bed recycle, with and without dilution (bed overflow water directed to the recycle tank) at 90 MW.

In general, results show:

1. The APCS can be run with above bed diluted recycle without scaling at or below stoichiometric additive feed rates.

2. Modifications are required (additional pump capacity) to fully test underbed recycle.

3. Dust efficiency is between 98.5 and 99.2 percent.

4. Overall SO_2 removal efficiency ranged from 50 to 75 percent depending on mode of operation.

Approximately 1500 hours of operating time was accumulated in 1971 up to mid-June 1971 despite a three week annual outage.

The Environmental Protection Agency ran a weeklong series of tests at our installation in Kansas in order to set national standards in terms of particulate and gaseous pollutant emissions.

Kansas Power and Light Lawrence #5

The unit has been in service since March, 1971, on gas operation. The APCS under went preliminary check-out in September, 1971. The unit was operated on a partial coal firing basis for five days prior to a scheduled one-month unit outage. It is presently planned to return the unit to service the week of November 15, 1971, at which time full coal operation will commence.

During the preliminary operation of the APCS at the end of September, two problems were observed.

Initial operation revealed poor gas distribution in the scrubbers. High velocities were found in the rear of the beds and conversely the front of the beds (side above the inlet) were not active. Tests on gas flow models at our research lab indicate that the installation of three ladder vanes will give the necessary improvement in gas distribution. These systems are currently being installed with a wash system to minimize deposition. This ladder vane assembly is a simplified version of those previously tried at Union Electric and KP&L Lawrence #4.

A second problem was encountered during this brief period of operation in September. The distribution of furnace injected limestone to the six scrubbers was found to be very poor. A modification to the limestone injection system is currently being made to improve the distribution of the additive in the furnace.

The correction of the imbalance in limestone addition at the point of intoduction should allow us to cope with small variations, the scrubbers by employing the recycle concept previously mentioned.

CONCLUSIONS

In summary, C-E is one of the pioneers in the development of methods to minimize emissions from stacks of power plants. For example, initial work on the C-E pollution control system for controlling SO_2 and dust emissions began some seven years ago at our Kreisinger Development Laboratory to meet the needs of our electric utility customers. The project was undertaken without government funding. Today, after the sale of a number of systems, our program is still going strong. Our efforts have been expanded and new areas are now being explored.

TABLE 1

AIR POLLUTION EMISSIONS

IN THE U.S. FOR 1969

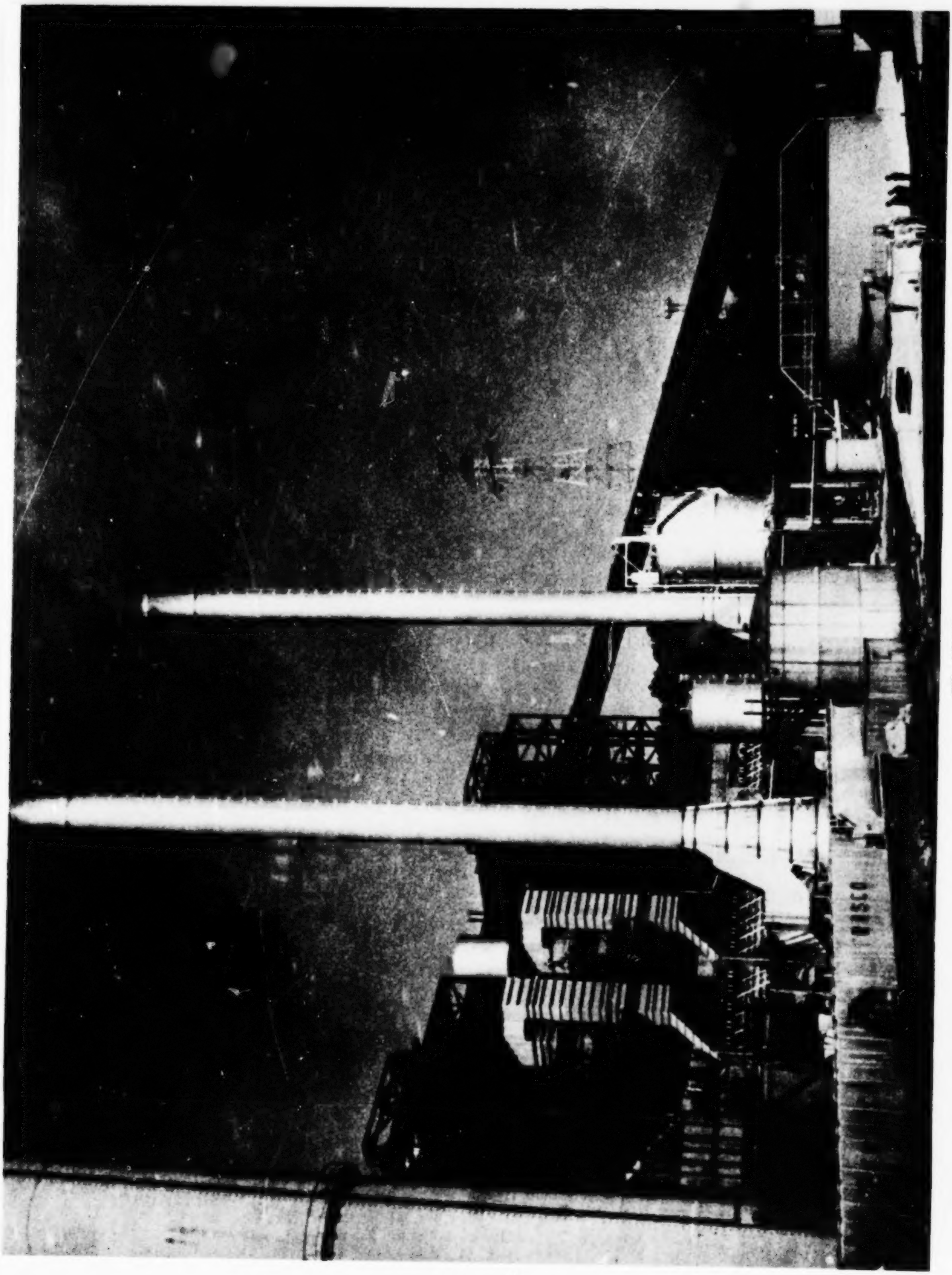
POLLUTANT	MILLIONS TON/YEAR	%
Sulfur Oxides	26	18.3
Nitrogen Oxides	13	9.2
Particulate Matter	12	8.4
Carbon Monoxide	72	50.7
Hydrocarbons	19	13.4

TABLE 2

COST COMPARISON OF CE WET SCRUBBING

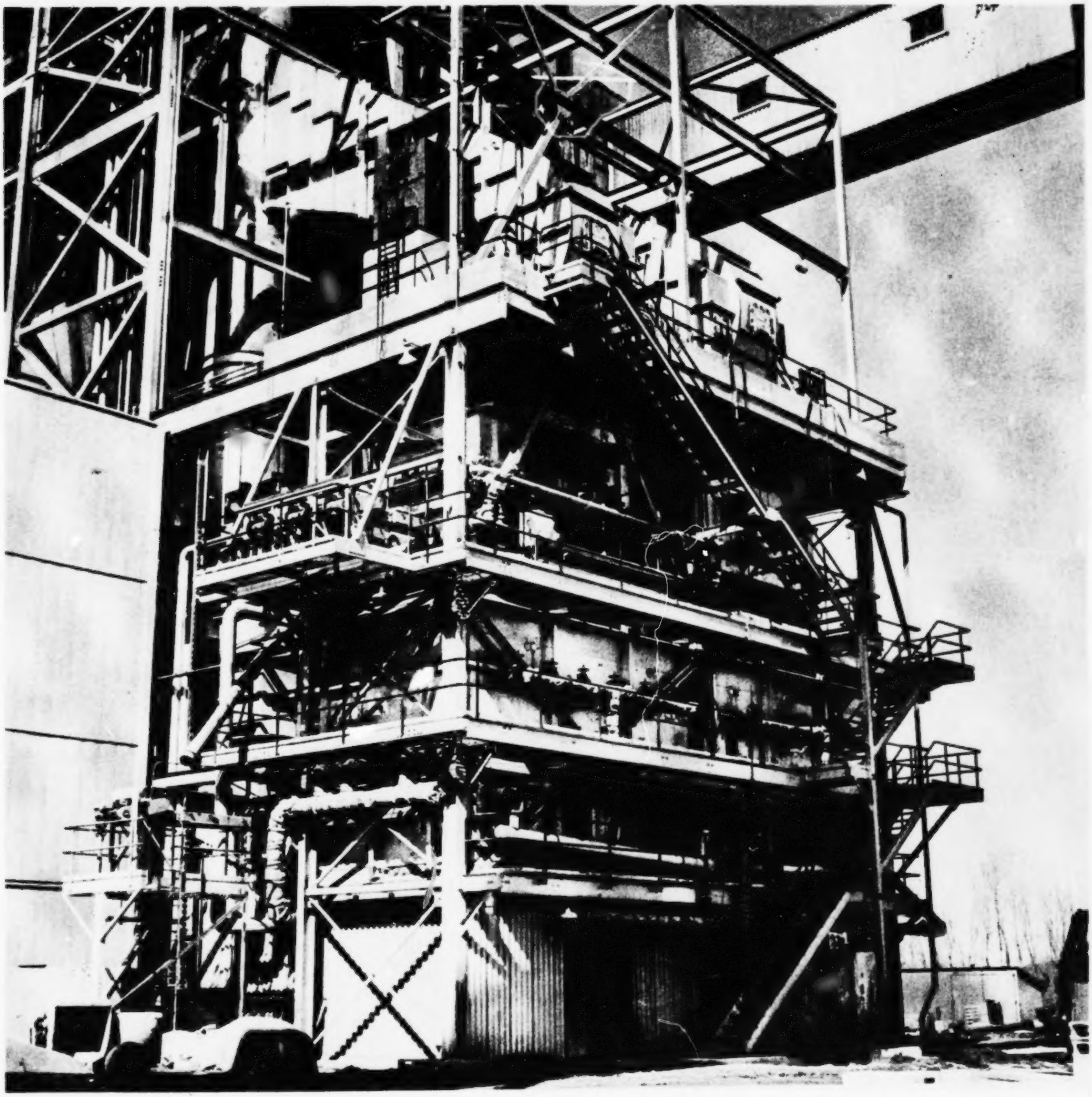
PROCESS VS SULFUR RECOVERY PROCESSES

PROCESS	CAPITAL COST $/KW	OPERATING COST MILLS/KWH
CE	13 to 25	0.2
Sulfur Recovery	30 to 60	0.7 to 1.5



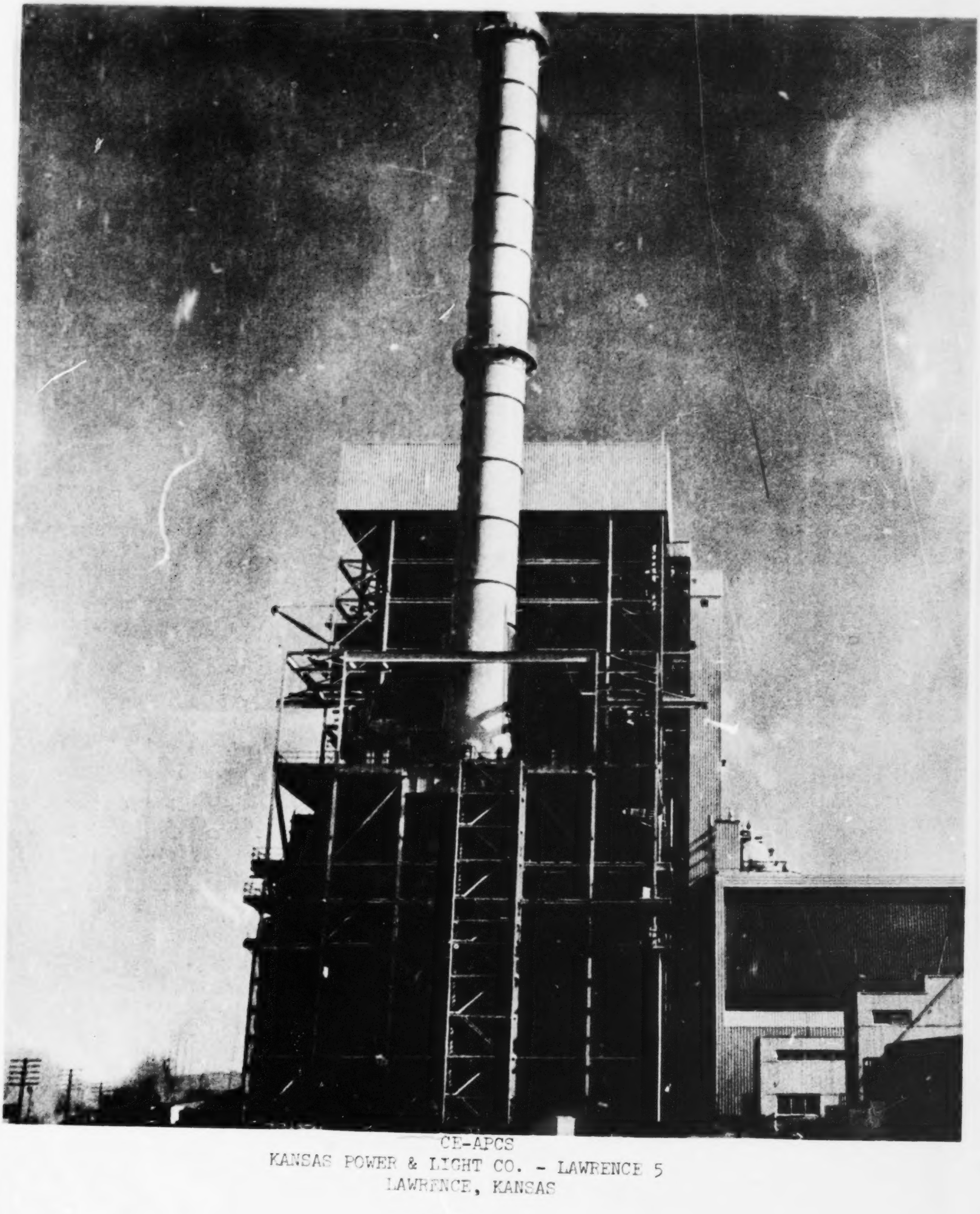
CE-APCS
UNION ELECTRIC CO.
ST. LOUIS, MISSOURI
MERAMEC 2

Fig. -1



CE-APCS
KANSAS POWER & LIGHT CO.
LAWRENCE, KANSAS
LAWRENCE 4

Fig. -2



CE-APCS
KANSAS POWER & LIGHT CO. - LAWRENCE 5
LAWRENCE, KANSAS

Fig. -3

REMOVAL OF SULFUR DIOXIDE FROM STACK GASES
BY SCRUBBING WITH LIMESTONE SLURRY:
DESIGN CONSIDERATIONS FOR DEMONSTRATION FULL-SCALE SYSTEM AT TVA

By

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Sponsored by the Environmental Protection Agency
New Orleans, Louisiana
November 8-12, 1971

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ABSTRACT

Design considerations are presented for the limestone slurry scrubbing system planned for TVA's Widows Creek unit 8 (550-mw; plant located in Northeast Alabama). The scrubber type will be selected on the basis of results from pilot plant tests. Basic design premises for the overall installation are given and the following major design factors are discussed.

- Limestone handling and grinding.
- Scrubber design (e.g., gas velocity, entrainment separation, turndown, liquor flow rate, limestone amount and particle size, solids content of slurry).
- Particulate removal.
- Equipment arrangement.
- Flue gas handling and conditioning.
- Instrumentation and control.
- Materials of construction (for resistance to both corrosion and erosion).
- Method of solids disposal.

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The Tennessee Valley Authority (TVA) has a major research and development program under way, mainly in cooperation with EPA, on methods for removing SO_2 from power plant stack gas. Small-scale and pilot plant work, plus the EPA-TVA large-scale test program at the TVA Shawnee Steam Plant, have been described in other papers in this symposium. In addition, TVA decided in late 1970 to install a full-scale SO_2 removal system on generating unit 8 at Widows Creek Steam Plant (in Northeast Alabama, near Chattanooga, Tennessee). The primary objective is to work out design and operating problems that affect both SO_2 removal efficiency and process reliability, with emphasis on the latter. Hopefully, a removal system can be designed and demonstrated that will serve as a model for any future installations required.

Among the reasons for selecting Widows Creek No. 8 as the demonstration unit was the fact that the electrostatic precipitators there are quite inefficient. Since additional dust removal capacity was needed anyway, it was decided to install a wet scrubbing process and thus remove both the residual dust and the SO_2. Thus the dust problem was a major factor in the decision to remove SO_2, which otherwise might have been delayed until design data were available from the EPA-TVA Shawnee project.

In selecting a process, the first choice to be made was between recovery and throwaway operation. Since no proven recovery methods were available, and marketing problems were considered quite difficult, throwaway was selected even though it involves a solid waste disposal problem.

The next choice was between lime and limestone as the absorbent. Lime is more active but can be produced economically only by injection of limestone into the boiler and catching the resulting lime in the scrubbers. Several major problems made this course unattractive:

1. Experience by TVA and others has shown that injection of limestone into the boiler can cause fouling and plugging of boiler surfaces and tube assemblies.

2. The use of lime, particularly when introduced with the gas, aggravates the scaling problem. Scaling can be reduced or eliminated by operating the scrubber at low pH or by high blowdown and replacement with fresh water. Both are undesirable, the latter particularly because it entails outflow of scrubber liquor to watercourses. It was decided that the TVA system must operate as a "closed loop," that is, with return of all liquor to the scrubber.

3. Since it was desired to retain the precipitators, the presence of lime in the gas from the boiler would have complicated operation.

4. Dry grinding of limestone creates a dust problem.

5. If lime is generated in the boiler, there is the problem of getting the same $CaO:SO_2$ ratio to all of the scrubbers serving the boiler.

It was decided, therefore, to introduce the limestone, after wet grinding, directly into the scrubber circuit. Experience by others has indicated that this reduces the scaling problem by a major degree. It also, of course, avoids the other problems listed for boiler injection.

An attempt is made in this paper to define and evaluate the design considerations associated with limestone scrubbing. Design areas considered are limestone handling and grinding, scrubber design, particulate removal, equipment arrangement, stack gas handling and conditioning, instrumentation and control, materials of construction, and method of solid disposal.

Figure 1 shows the general area at the Widows Creek Steam Plant, with the expected location of equipment. The new waste solids pond is also shown.

Basic Design Premises

In preliminary planning for the scrubbing facility, it was first necessary to establish major design premises. The more important of these are as follows:

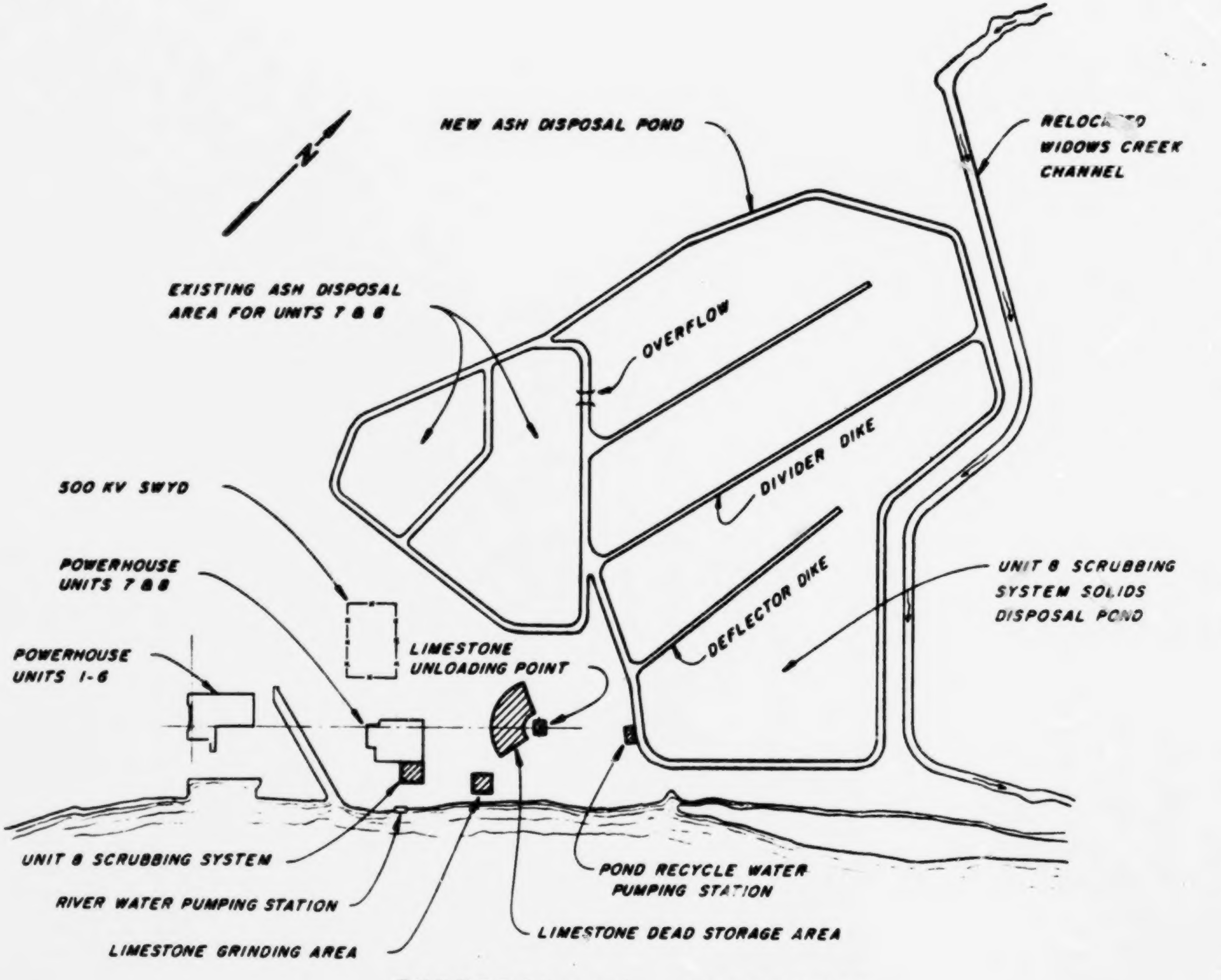
NEW ASH DISPOSAL POND
N
RELOCATED
WIDOWS CREEK
CHANNEL
EXISTING ASH DISPOSAL
AREA FOR UNITS 7 & 8
OVERFLOW
DIVIDER DIKE
DEFLECTOR DIKE
500 KV SWYD
POWERHOUSE
UNITS 7 & 8
UNIT 8 SCRUBBING
SYSTEM SOLIDS
DISPOSAL POND
POWERHOUSE
UNITS 1-6
LIMESTONE
UNLOADING POINT
UNIT 8 SCRUBBING SYSTEM
POND RECYCLE WATER
PUMPING STATION
RIVER WATER PUMPING STATION
LIMESTONE DEAD STORAGE AREA
LIMESTONE GRINDING AREA
GUNTERSVILLE RESERVOIR

FIGURE 1

1. Coal analysis (as fired basis)
    a. Ash content, 25%
    b. Sulfur content, 4.3%
    c. Moisture, 5.0%
    d. Heating value, 10,000 Btu/lb
2. Capacity
    a. Maximum power generation rate for unit No. 8, 550 mw
    b. Stack gas rate at capacity,[1] 1,600,000 acfm at 280°F (5,325,000 lb/hr)
3. Sulfur dioxide removal
    a. Percent removal, 80
    b. Inlet concentration, 3440 ppm (wet basis); 3740 ppm (dry basis)
    c. Outlet concentration, 650 ppm (wet basis); 750 ppm (dry basis)
4. Particulate removal
    a. Inlet particulate loading,[2] 5.6 gr/scf (dry); 5.1 gr/scf (wet); 3.6 gr/acf (280°F)
    b. Particulate level at scrubber exit,[2] 0.020 gr/acf (125°F saturated); 0.022 gr/scf (wet); 0.026 gr/scf (dry)
5. Stack gas reheat temperature, 175°F (50°F rise)

These premises have been used for preliminary engineering purposes but will be reviewed and updated as required prior to detailed engineering.

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[1] Based on a total of 33% excess air including air heater leakage.
[2] Based on the conventional ASME sampling technique.

Limestone Handling and Grinding

A wet grinding system for limestone was chosen over dry grinding because it is less expensive and does not produce a dust problem. Even if dry grinding were used, the ground limestone probably would be slurried before feeding to the scrubber.

A schematic drawing of the limestone handling and grinding system is shown in Figure 2. The facility is designed for receiving limestone by both rail and truck from the quarry. The limestone is conveyed from an unloading hopper to either the live storage silo or the dead storage area. Material will be reclaimed from the dead storage area as required to maintain an adequate level in the live storage silo. Capacity of the latter is sufficient for 3 days' operation.

Limestone is conveyed from the live storage silo to a wet ball mill where it is ground from the purchased size (probably 1-1/2 by 0 in.) to the desired size. The resulting slurry is pumped from the ball mill through a classifier where the oversized particles are separated and recycled to the ball mill. The product slurry (50-60% solids) from the classifier goes to a hold tank from which it is pumped to the scrubbing system.

Final selection of the particle size has not been made, but it will not likely be coarser than 70% minus 200 mesh or finer than 90-95% minus 325 mesh. Selection of the size will be made after completion of additional pilot plant tests. Hopefully, the additional tests will produce sufficient data to permit determining whether the advantages of a finer grind justify the increased grinding cost. The potential advantages are primarily (1) less erosion of piping and equipment and (2) less limestone requirement for a given SO_2 removal rate, other conditions being equal.

Final selection of limestone feed stoichiometry has also not yet been made but probably will be between 1.2 and 1.5. The final selection will depend upon results of additional pilot testing and selection of a particle size.

The limestone source probably will be deposits in the vicinity of the Widows Creek plant. Estimates have indicated that the cost of shipping limestone from greater distances would not be economical unless some major advantage could be demonstrated, which has not yet been done. The local deposits are fortunately quite low in magnesium, which could cause a ground water pollution problem if present in large amounts. The composition of the limestone is given in another paper in this symposium ("Removal of Sulfur Dioxide from Stack Gases by Scrubbing with Limestone Slurry: TVA Pilot Plant Tests--Part I, Scrubber-Type Comparison" by T. M. Kelso, P. C. Williamson, and J. J. Schultz).

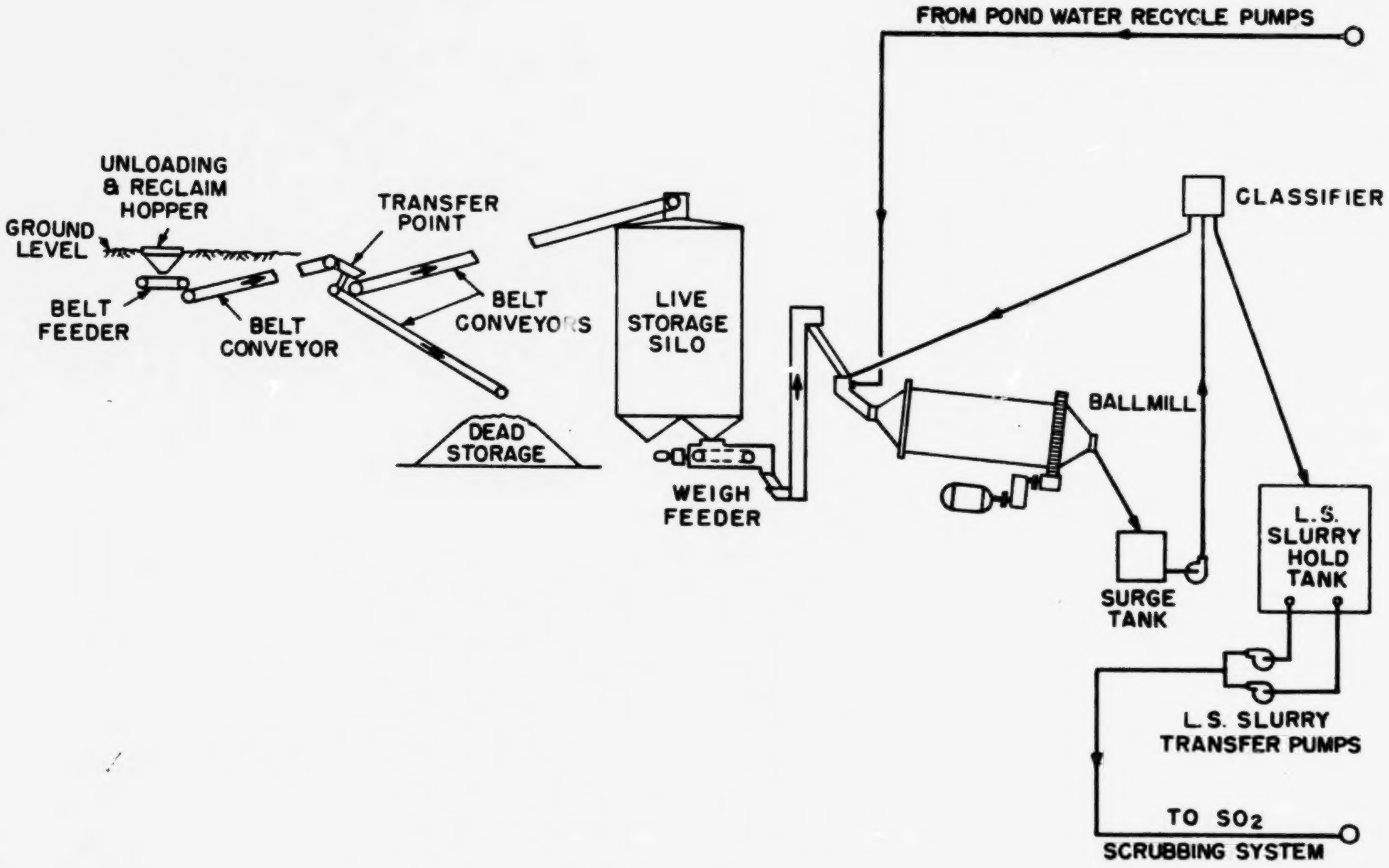

FIGURE 2

Limestone Handling and Grinding System

The flowsheet shows recycled pond water as the liquid portion of the mill feed. Use of recycled water at this point reduces the amount available for washing the mist eliminators in the scrubber, for which a substantial flow of clear liquid is needed. Further attention will be given to the problem of portioning out the available clear liquor for the various needs.

Scrubber Design

Several scrubber designs and configurations for limestone scrubbing have been considered in studies conducted at TVA. Three types remain under consideration for the Widows Creek facility: (1) a venturi - spray tower system, (2) a venturi - mobile-bed combination, and (3) the mobile-bed type alone. Flow diagrams for the three are given in Figures 3, 4, and 5. In each of the three schemes, four scrubber trains will be used--one for each of the four stack gas ducts from the boiler.

In the venturi - spray tower system (Fig 3), the gas exiting the electrostatic precipitator is cooled and presaturated prior to entering the absorption tower. The latter is an open spray tower equipped with a venturi in the bottom of the tower. The venturi, through which a portion of the scrubber circulating slurry is injected, serves to remove fly ash and to atomize the scrubbing liquor for SO_2 absorption. The remaining circulating slurry is injected into the top portion of the spray tower through spray headers equipped with nozzles.

Under the current plan, limestone slurry from the mill, recycled pond water, and makeup river water are introduced into the absorber circulation tank (however, as mentioned earlier, it may be necessary to use all available water and clear liquor to wash the mist eliminators). The resulting slurry is circulated from the tank through the presaturator, venturi, and the two spray tower headers, with liquid to gas ratios (L/G) of about 7, 20, 20, and 20 gal/Mcf, respectively, to the four points.

The pressure drop across the venturi is 10-15 in. H_2O. Recent pilot tests indicate that a lower pressure drop than this is adequate for dust removal. However, the tests also indicate that the higher pressure drop is necessary for adequate SO_2 removal in the venturi, presumably because the pressure drop gives a more effective spray pattern in the lower part of the scrubber.

The superficial design velocity for the spray tower is 6-8 ft/sec, and the solids content of the circulating slurry is 10-15% by weight.

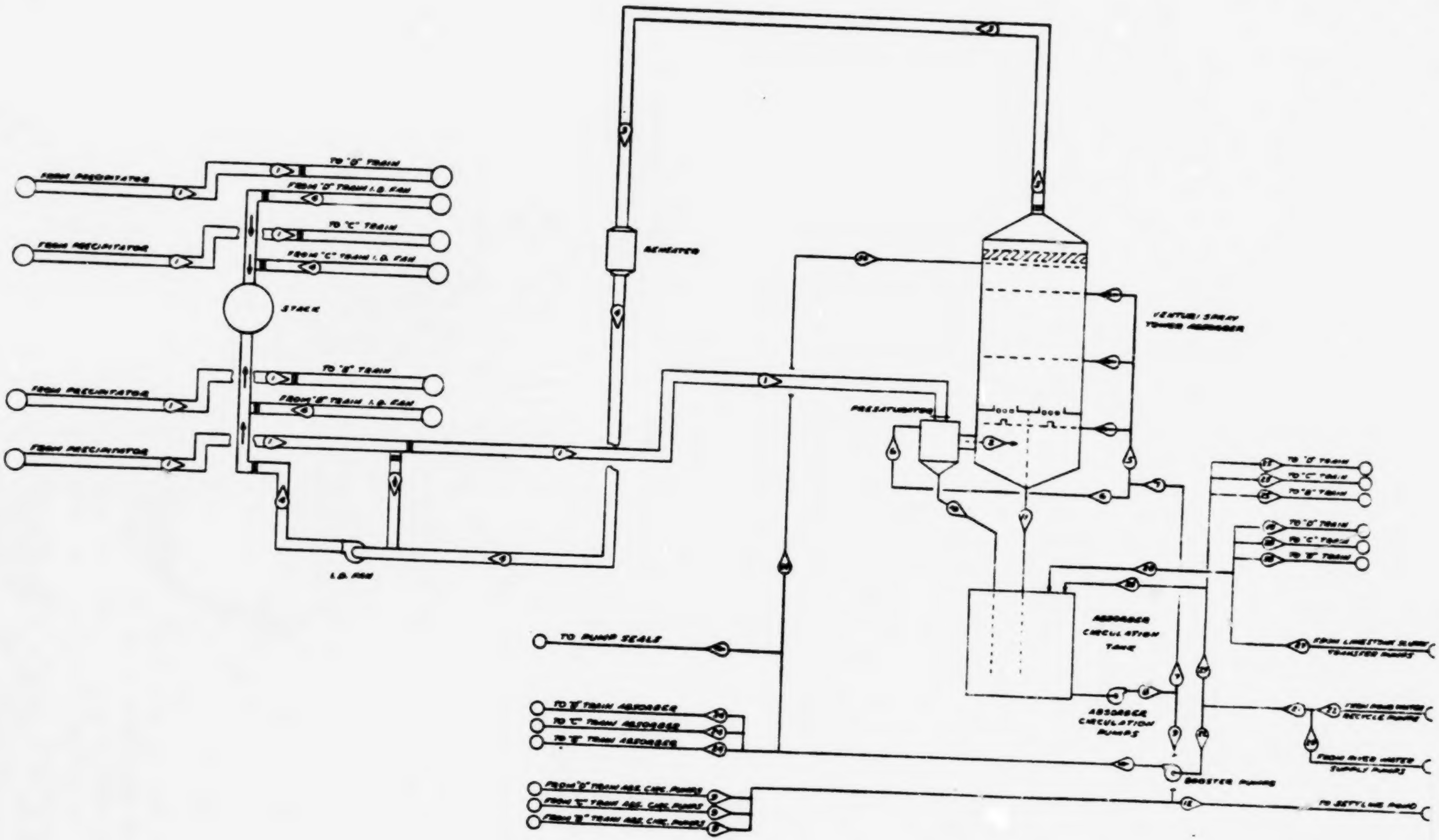

FIGURE 3

Venturi - Spray Tower System Flow Diagram

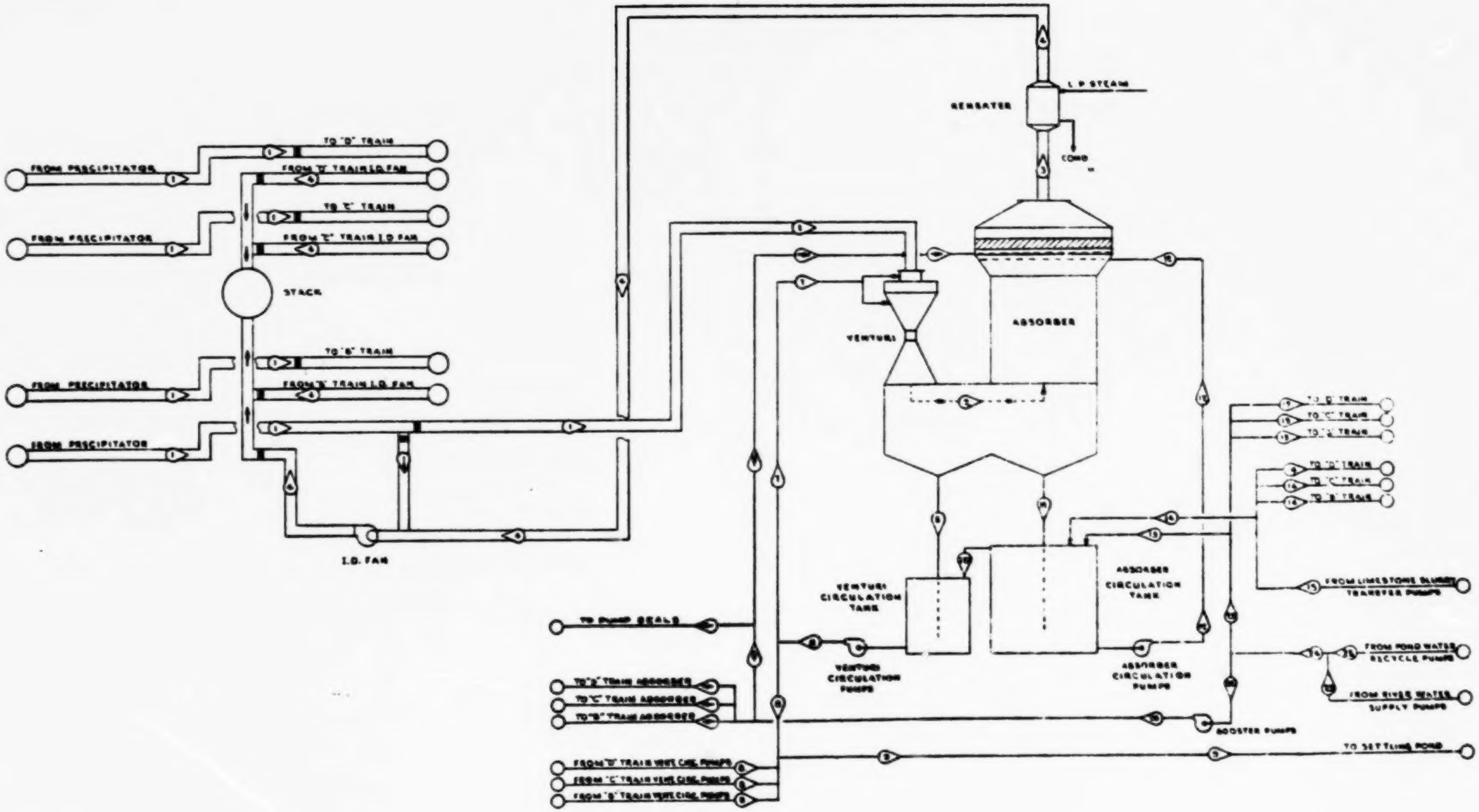

FIGURE 4

Venturi - Mobile-Bed System Flow Diagram

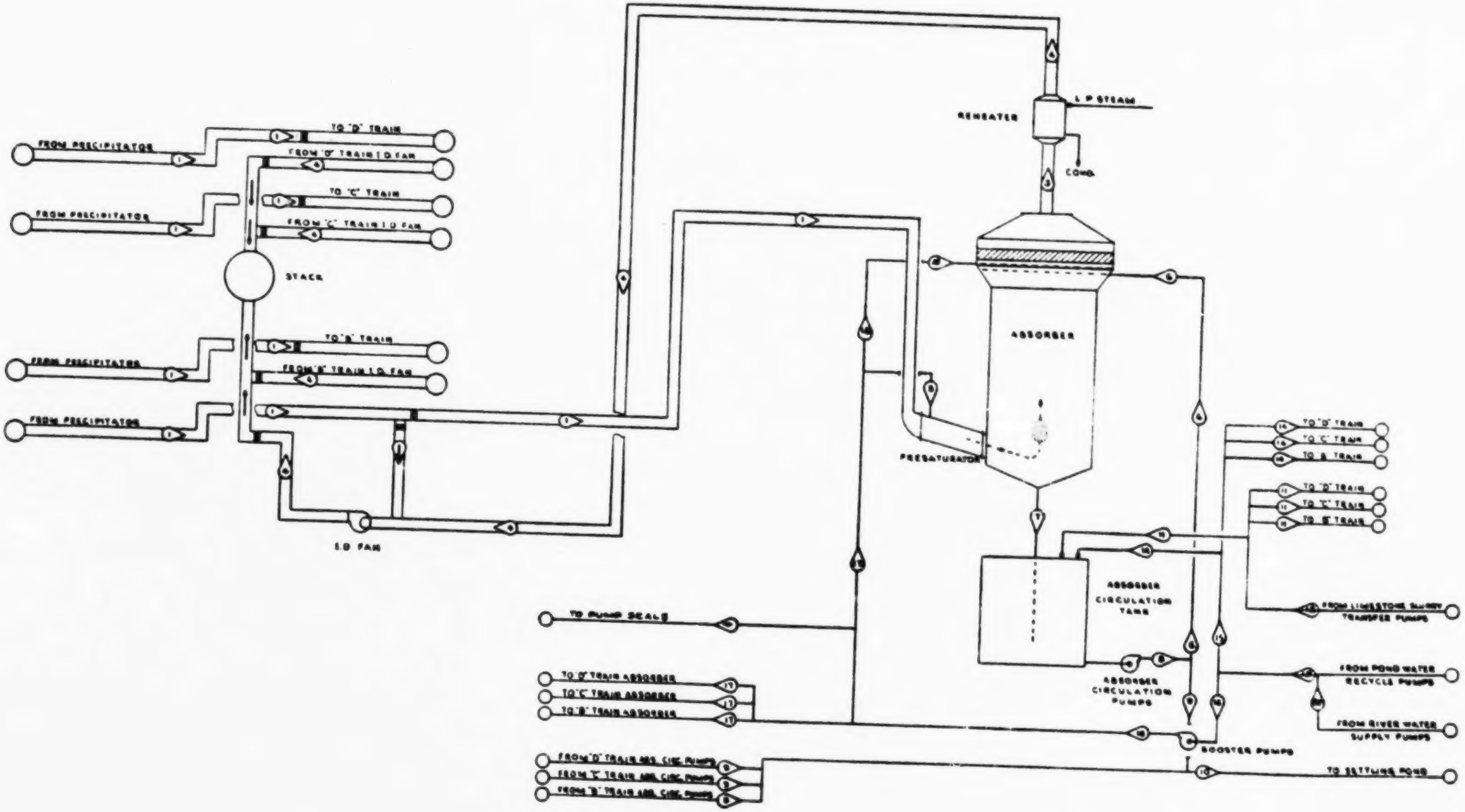

FIGURE 5

Mobile-Bed System Flow Diagram

In the venturi - mobile-bed system (Fig 4), stack gas from the electrostatic precipitators enters the venturi where it is cooled, saturated, and the fly ash removed. The cooled gas then flows to the mobile-bed scrubber where the SO_2 is absorbed. Limestone slurry and recycled pond water (see earlier discussion) are added to the absorber circulation tank. Slurry is circulated from this tank to the upper of the two beds through a spray nozzle header (low pressure) and flows down through the scrubber. Slurry overflows from the absorber circulation tank to the venturi circulation tank from which it is circulated through the venturi.

The absorber is operated with a liquid:gas ratio of about 40 gal/Mcf and a pressure drop of about 6-8 in. H_2O. Corresponding values for the venturi are 20 L/G and 4-5 in. H_2O. The superficial design velocity in the mobile-bed scrubber is 12-13 ft/sec. The solids content in the circulating slurries has been set tentatively at 5 and 8%, respectively, for the mobile bed and the venturi. The 5% was selected because general practice is to avoid higher contents in order to limit wear of the plastic balls. However, the pilot plant has been operated at 10-15% solids to reduce scaling, improve SO_2 removal, and reduce pumping load for transporting the waste solids to the pond and the separated liquor back again. Finer limestone particle size may allow use of the higher solids content without excessive ball wear; this is being tested in the pilot plant.

In the scheme involving use of mobile beds alone (Fig 5), the flue gas is cooled and saturated in a spray chamber presaturator before entering the mobile-bed scrubber, which removes both fly ash and SO_2. Limestone slurry and recycle pond water are added to the absorber circulation tank from which the slurry is circulated to the upper of the three beds through a spray header and flows down through the other beds.

The absorber is operated at an L/G of 40-50 gal/Mcf and 9-12 in. H_2O pressure drop. An L/G of about 5 is used for the presaturator. The absorber superficial gas design velocity is 12-13 ft/sec.

The three beds are specified because this was the arrangement tested in the pilot plant. There is some evidence from the pilot plant work, however, that the upper bed contributes very little to SO_2 removal. Further tests will be made in an effort to find the best combination.

In each of the three scrubber arrangements, the absorber is equipped with an entrainment separator. Provisions will be made for continuous or intermittent flushing with recycled pond water. The selection of the entrainment separator is further discussed later under the problem of particulate removal.

Some of the advantages and disadvantages of each of the three schemes are as follows:

1. The venturi - spray tower has a lower superficial gas velocity, which results in a larger scrubber cross-sectional area than the other two schemes.
2. Erosion of the plastic spheres in the two schemes using mobile beds is a major potential problem.
3. The turndown capacity of the mobile-bed scrubber is limited, which may lead to pluggage and other problems at reduced loads. Also, fly ash removal may be a problem at reduced load in use of the mobile-bed scheme in which the scrubber must remove both fly ash and SO_2.
4. For the large cross-sectional areas involved, there may be the problem of poor sphere distribution in use of the mobile beds. It may be possible to keep the spheres in place by use of vertical partition screens but this has not been proven in practice.
5. The higher gas velocity in the mobile bed results in a higher loading on the entrainment separator.
6. The mobile-bed scrubber is a better contacting device than the spray tower, which gives better SO_2 removal efficiency or possibly a lower limestone consumption rate.
7. Spray nozzle erosion is more severe in the venturi - spray tower combination because spray nozzles with higher pressure drop are required.
8. A higher pressure head on the pumps is required for the venturi - spray tower system.
9. The venturi - mobile-bed system is the most flexible of the three because dust and SO_2 removal units are separated.

Alterations to the configurations of the above schemes are under consideration that may have potential advantages.

1. Packed section in spray scrubber. A short, open packed section in the upper part of the spray tower should increase SO_2 removal and perhaps be free of scaling if open enough.

2. The three-bed TCA scrubber performed fairly well in the pilot plant with the balls removed. Thus a scrubber with several horizontal, open, thin grids (similar to the retaining grids in the TCA scrubber) spaced from the scrubber top to bottom, might give adequate SO_2 removal without the problems associated either with the usual type of fixed packing or with the mobile-bed type of scrubber.

The choice between the various scrubber schemes will be made after completion of additional pilot plant tests. The investment and operating costs of the three will be compared before a decision is made; preliminary estimates, however, indicate little difference among them. It is likely that the primary factor influencing the final selection will be the experience gained regarding operating reliability.

Particulate Removal

Pilot tests conducted at Widows Creek on unit 8 stack gas indicate that the fly ash can be removed satisfactorily with a pressure drop of 4-5 in. H_2O and relatively low liquid:gas ratios, about 10-15 gal/Mcf. The main problem, as discussed earlier, is entrainment of slurry solids into the gas stream. Thus development of efficient mist elimination equipment is essential for the Widows Creek project.

In most of the pilot plant tests to date, a vane-type entrainment separator has been used--selected because of low pressure drop and large open area which minimizes pluggage and is easy to flush. Plugging and poor efficiency have been major problems. Further studies will be conducted to determine the best type of entrainment separator for the scrubbers at Widows Creek. One course being explored is use of two mist eliminators in series, the first irrigated with clear liquor to replace slurry mist with clear liquor mist and the second to remove the clear liquor mist. Use of the upper TCA bed, which apparently does not contribute much to SO_2 removal, as a mist eliminator may also be helpful since the movement of the balls should prevent plugging. Also, if a fixed-bed section in the top of the scrubber should prove feasible, mist carryover probably would be reduced.

Equipment Arrangement

A typical equipment arrangement study drawing is shown in Figure 6. The general arrangement will be similar for each of the three scrubber schemes under consideration. Detailed equipment arrangement drawings will be made after a specific scrubber scheme is chosen.

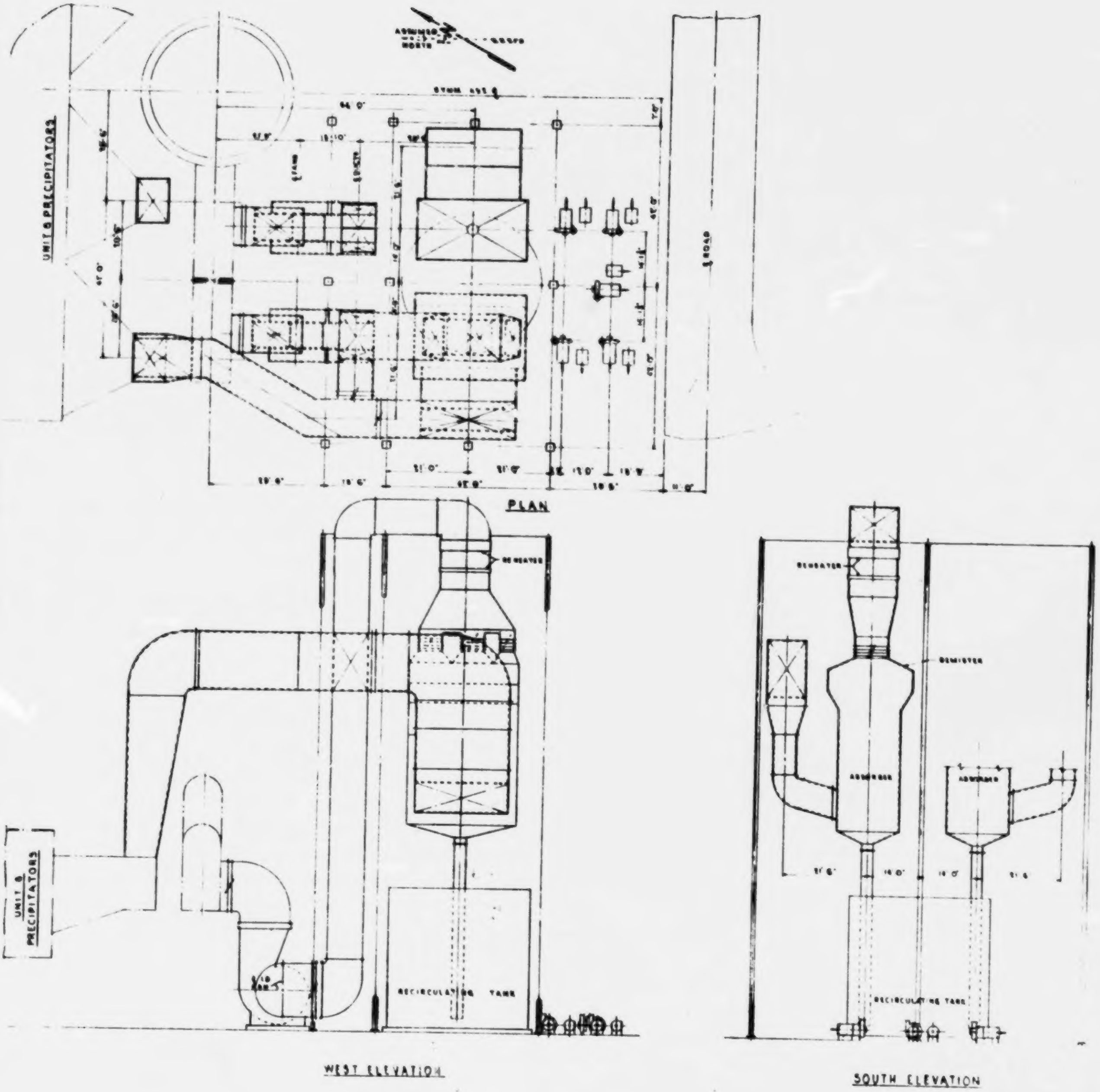

FIGURE 6

General Arrangement Study

The general plot plan shown in Figure 1 shows the relative location of the three major areas (scrubbing system, limestone handling-grinding, and solids disposal) with respect to each other and the unit 8 powerhouse.

Stack Gas Handling and Conditioning

As noted earlier, the gas will be humidified and cooled prior to entering the SO_2 absorber. Cooling the gas prior to the absorber is desirable primarily for two reasons: (1) better SO_2 absorption and (2) elimination of temperature problems in materials selection for the absorber. The gas entering the absorber will be cooled to a temperature of 150°F or less.

The gas leaving the scrubber will be reheated to desaturate and to provide buoyancy. The reheater will be designed to provide up to 50°F temperature rise (125-175°F). Both direct reheating by burning oil and indirect heating with low pressure steam are being considered. Primary consideration is being given to indirect steam but no decision can be made until the economics are further evaluated.

Soot blowers or liquor sprays will be installed where there is a likelihood of deposits forming, particularly in the presaturator and the reheater wet-dry interface areas.

The gas will be moved through the system by induced-draft fans located downsteam of the reheaters to permit operation of the fans with a "clean" unsaturated gas. Consideration is being given to designing the fans with sufficient static pressure to permit converting the boilers from the present pressure type to balanced draft. A plenum will be provided connecting the four ducts to the scrubbers to permit operation of the boiler up to 75% load with one scrubbing train out of service. Also, bypasses will be provided around the scrubbers to the stack to prevent an undue amount of boiler downtime because of scrubber malfunction, particularly during the initial shakedown operation of the system.

Provision for scrubber turndown is a potential problem. If the individual scrubbers cannot be turned down without operating difficulty, then provision must be made to cut one or more scrubbers out of the system at low boiler load so as to maintain adequate gas velocity through the active scrubbers. This could require frequent operator attention to cut scrubbers in and out of the system and would put emphasis on finding dampers that open and close easily, are resistant to sticking, and close tightly.

Instrumentation and Control

In general, the scrubbing system will be well instrumented to permit flexibility in control and monitoring of the system since it will be a demonstration unit. Also, adequate controls are required to minimize operating personnel requirements.

Since there are four similar trains, one of them will have more instrumentation than the others to permit flexibility in determining optimum operating conditions. In addition to being useful in optimizing the Widows Creek facility, this should give data useful in design and operation of any subsequent installations.

Operating variables to be controlled include limestone feed rate to the scrubber and solids concentration in the circulating scrubber slurry. The limestone rate will be regulated to maintain the desired stoichiometry, either directly or indirectly. The solids content of the slurry will be maintained at the desired level by regulating the slurry purge rate to the pond. Additional considerations on instrumentation and control of the system are as follows:

1. The induced-draft fans will be instrumented and controlled similarly to induced-draft fans for balanced draft furnaces.
2. Analyzers will be provided for monitoring the scrubbing system inlet and exit SO_2 concentrations.
3. One of the four trains will be equipped for regulating the slurry circulation rate to the scrubber. Amperage recorders will be provided for the scrubber circulation pumps on all four trains for rough monitoring of liquid circulation rates.
4. Sampling points, temperature recorders, pressure and differential pressure recorders, etc., will be provided as deemed necessary for monitoring and controlling the system.

Materials of Construction

Selection of the most economical materials for adequate resistance to corrosion-erosion is a major problem. Attempts have been made in the pilot plant to evaluate various materials of construction including metals, coatings, and linings. However, it is very difficult to obtain conclusive corrosion-erosion data in the pilot plant because of the short running time of the tests. Evaluation of coatings and linings is particularly difficult.

The equipment items most susceptible to erosion-corrosion are pumps, piping, nozzles, and areas where there is slurry impingement against surfaces. Corrosion is generally not thought to be very severe in the system except for its enhancement by erosion. The material that appears to be most promising for the high erosive areas is carbon steel lined with a soft elastomer such as neoprene with a 55-60 Shore A hardness. However, in addition to being expensive, neoprene-lined carbon steel has some distinct disadvantages; field modifications and repairs are difficult, expensive, and time consuming. Such linings also generally have a maximum allowable continuous operating temperature of only about 150°F.

For tanks where erosion is not as severe, carbon steel lined or coated with a less expensive material than neoprene should be satisfactory. It may also be feasible to use unlined steel, as was done in the early ICI work in England--particularly where the pH is above 6.0.

Solids Disposal and Water Recycle

The solids purge stream will be pumped to the pond without any concentration of the solids. The supernatant clear liquor will be recycled from the pond to the scrubbing system for reuse. River water makeup will be used as necessary to maintain the water balance in the system. Water is lost from the system by evaporation in the scrubber, hydration of reaction products, pond water evaporation, pond seepage, and entrainment with settled solids as interstitial water. Water enters the system as rainfall into the pond and as river water makeup to the scrubber. An overall water balance is given in another paper in this symposium ("Removal of Sulfur Dioxide from Stack Gases by Scrubbing with Limestone Slurry: Operational Aspects of the Scaling Problem" by A. V. Slack and J. D. Hatfield).

Thickeners could be used to concentrate the purge slurry and reduce the pumping rates to and from the pond. However, the savings in pumping costs do not justify the additional capital investment required for thickeners. Also there is some doubt as to how effective thickeners would be in concentrating the purge slurry because of the very poor settling characteristics of the product solids.

One of the undesirable aspects of the solids disposal system is the possible low bulk density of the settled solids in the pond. Data from the TVA pilot plant indicate that the settled solids contain about 50-60% by weight water. The corresponding bulk density is 89-82 lb/ft^3 of slurry, which results in a large pond volume requirement for storing the accumulated solids. Further work is planned aimed at reducing the settled solids volume.

TEST PROGRAM FOR THE EPA ALKALI SCRUBBING TEST FACILITY AT THE SHAWNEE POWER PLANT

By

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INTRODUCTION

In June, 1968, a three phase program was initiated whose aim was the testing of a large, versatile prototype system to fully characterize wet limestone scrubbing for removal of sulfur dioxide and particulates from boiler flue gas. The Office of Air Programs (OAP) of the Environmental Protection Agency (EPA) is sponsoring this program, with Bechtel Corporation of San Francisco as the major contractor.

Phase I of the test program, which has been completed, consisted of preliminary engineering, equipment evaluation and site selection. Phase II, which is close to completion, involves the detailed design and construction of the facility and the development of the test-plan and mathematical models for predicting system performance. Phase III will comprise, primarily, the testing portion of the program.

The test facility consists of three parallel scrubber systems, each capable of treating approximately 30, 000 acfm of flue gas, which are integrated into the flue gas ductwork of an existing coal-fired boiler at the Tennessee Valley Authority (TVA) Shawnee Power Station, Paducah, Kentucky. The facility was designed for maximum flexibility and has a high degree of instrumentation for control and recording of data over a wide range of operating conditions. Construction is approximately 80% complete, with Phase III start-up presently scheduled for March 1972.

EPA has utilized the capabilities of several organizations to maximize the efficacy of the total program. For example, Bechtel Corporation, as the major contractor, has prepared the detailed design of the test facility, is developing the test program and mathematical models and will direct the test efforts. TVA is constructing the facility and will operate the unit during the test program. Other contributors include, Radian Corporation, who has provided important support in the analytical determination areas, and McCrone Associates, who participated in the development of the particulate mass loading and size distribution measurement procedures.

TEST PROGRAM OBJECTIVES

The overall objective of this program is to evaluate the feasibility and economics of closed-loop limestone wet-scrubbing processes. The following are the major goals of the program:

- Investigate and solve operating and design problems, such as scaling, plugging, corrosion and erosion.
- Generate test data to characterize scrubber and system performance as a function of the important process variables.
- Study various solid disposal methods.
- Develop mathematical models to allow economic scale-up of attractive operating configurations to full-size scrubber facilities. A parallel economic study will be performed to enable estimation of capital and operating costs for the scaled-up system designs.
- Determine optimum operating conditions for maximum SO_2 and particulate removal, consistent with operating cost considerations.
- Perform long-term reliability testing.

TEST FACILITY

The following discussion provides a brief description of the test facility. Reference 1 provides a recent, more complete description.

The test facility consists of three parallel scrubber systems, each with a different scrubber design and its own slurry handling system. Scrubbers will be of prototype size, each capable of treating approximately 30,000 acfm of flue gas from the TVA Shawnee coal boiler #10. Therefore, each circuit is handling the equivalent of approximately 10 Mw of power plant generation capacity. The equipment selected was sized for minimum cost consistent with the ability to extrapolate results to commercial units. The 30,000 acfm scrubber train was judged to meet these requirements.

SCRUBBER SELECTION

The major criterion for scrubber selection was the capability of removing both sulfur dioxide and particulates with high efficiency (sulfur dioxide removal greater than 85% and particulate removal greater than 99%). Other factors considered in the selection of the scrubbers were:

- Ability to handle slurries without plugging or excessive scaling.

- Cost and maintenance requirements.
- Ease of control.
- Pressure drop.

Based on the limited information available in the literature, the following scrubbers were selected:

(1) Venturi followed by an after-scrubbing absorption section (spray or pall-ring packed-bed).

(2) Turbulent contact absorber (TCA).

(3) Marble-bed absorber (Hydro-Filter)

The venturi (manufactured by CHEMICO) contains an adjustable plug, which permits control of pressure drop under a wide range of flow conditions. The TCA (manufactured by UOP and described in Ref. 2) utilizes a packing of low density plastic spheres which are free to move between retaining grids. The Hydro-Filter (manufactured by National Dust Collector Corporation and described in Ref. 3) utilizes a packing of glass spheres (marbles) which are normally in slight vibratory motion. A "turbulent layer" of liquid and gas above the glass spheres increases mass transfer and particulate removal.

Models describing pressure drop, particulate and sulfur dioxide removal within the three scrubbers have been presented in Ref. 4.

SYSTEM FLEXIBILITY

The test facility has been designed to achieve great flexibility:

- The three scrubbers can be tested in parallel.
- Scrubber internals and piping configurations can be changed. For example, the TCA can be operated as a one, two or three stage unit, with a variety of liquor flow piping arrangements.
- The facility can be operated under various alkali addition modes. These include: limestone in the scrubber circuit, hydrate in the scrubber circuit and limestone (or dolomite) injection in the boiler. For the scrubber circuit addition modes, alkali can be added at two locations, the Scrubber Effluent Hold Tank or the Process Water Hold Tank.
- Various solid disposal configurations can be evaluated. They include: Clarifier/Pond
  Clarifier/Centrifuge/Pond
  Clarifier/Filter/Pond
- Each scrubber has been furnished with a quench spray to permit humidification and cooling of the flue gas prior to contact with the scrubbing slurry.
- A heat exchanger has been provided to permit cooling of inlet scrubber liquor (only one scrubber at a time).
- Each scrubber has its own oil-fired reheater (and stack) to increase the temperature of the exit gas over wet-bulb values.
- Each scrubber will accommodate either a chevron or centrifugal mist eliminator (demister).

SYSTEM RELIABILITY

Difficulties in achieving reliable operation of wet limestone scrubbing systems attributable to scaling, plugging, erosion and corrosion have been reported by many investigators.

The following are among the design and test features included to maximize system reliability:

- The scrubbers are either of stainless steel or Neoprene-lined carbon steel construction.
- All major piping, pumps and tanks are lined with rubber or fiberglass reinforced polyester.
- Variable speed pumps have been selected, where practicable, for flow control to avoid the solids build-up which can be produced by throttling flow controllers.
- Sootblowers have been installed at each scrubber inlet to minimize solids deposition.
- The flue gas has been heated downstream of the induced draft fan to reduce solids deposition within the fan.
- The ability to operate over a wide range of independent variables has been designed into the facility, to increase the likelihood of achieving operating conditions which are free of scaling and other operational problems.
- Scrubbers have been selected which are relatively immune to plugging and are designed to minimize solids build-up at liquid contact zones.

SYSTEM DESCRIPTION

Typical schematic flow diagrams for the Venturi, TCA and Hydro-Filter systems are shown in Figures 1, 2 and 3, respectively. Not shown are flue gas saturation sprays, heat exchanges for cooling of liquor, flow controls, and process details. These figures are intended to illustrate the range of operating conditions possible at the test facility.

In Figure 1, a venturi system is shown with a packed-tower (Pall-ring) after-scrubber, with hydrate ($Ca(OH)_2$) addition to the Scrubber Effluent Hold Tank and a Clarifier/Pond combination for waste disposal.

In Figure 2, a TCA system is shown with the TCA in a three-stage configuration, with limestone addition to the Scrubber Effluent Hold Tank and a Clarifier/Filter/Pond combination for waste disposal. In Figure 3, a Hydro-Filter system is shown with limestone addition to the boiler and a Clarifier/Centrifuge/Pond combination for waste disposal. Any of the scrubber systems can be operated with any of the solids disposal systems and with several piping flow configurations.

For all configurations, gas will be withdrawn from the boiler ahead of the power plant particulate removal equipment so that the entrained dust, including lime during injection-scrubbing tests, can be introduced into the scrubber. Gas flow rate to each scrubber will be measured by venturi flow tubes and controlled by dampers on the induced-draft fans. Concentration of sulfur dioxide in the inlet and outlet gas will be determined continuously. The efficiency of the process for removal of nitrogen oxides also will be determined by periodic checks of inlet and outlet concentration.

Control of the scrubbing systems will be carried out from a central graphic panelboard. An electronic data acquisition system will be utilized to record the operating data. The system is hard wired for data output in engineering units directly on magnetic tape. Onsite display of selected information will be available. Also, important process control variables will be continuously recorded and trend recorders will be provided for periodic monitoring of selected data sources.

Figure 1

TYPICAL PROCESS FLOW DIAGRAM FOR VENTURI SYSTEM

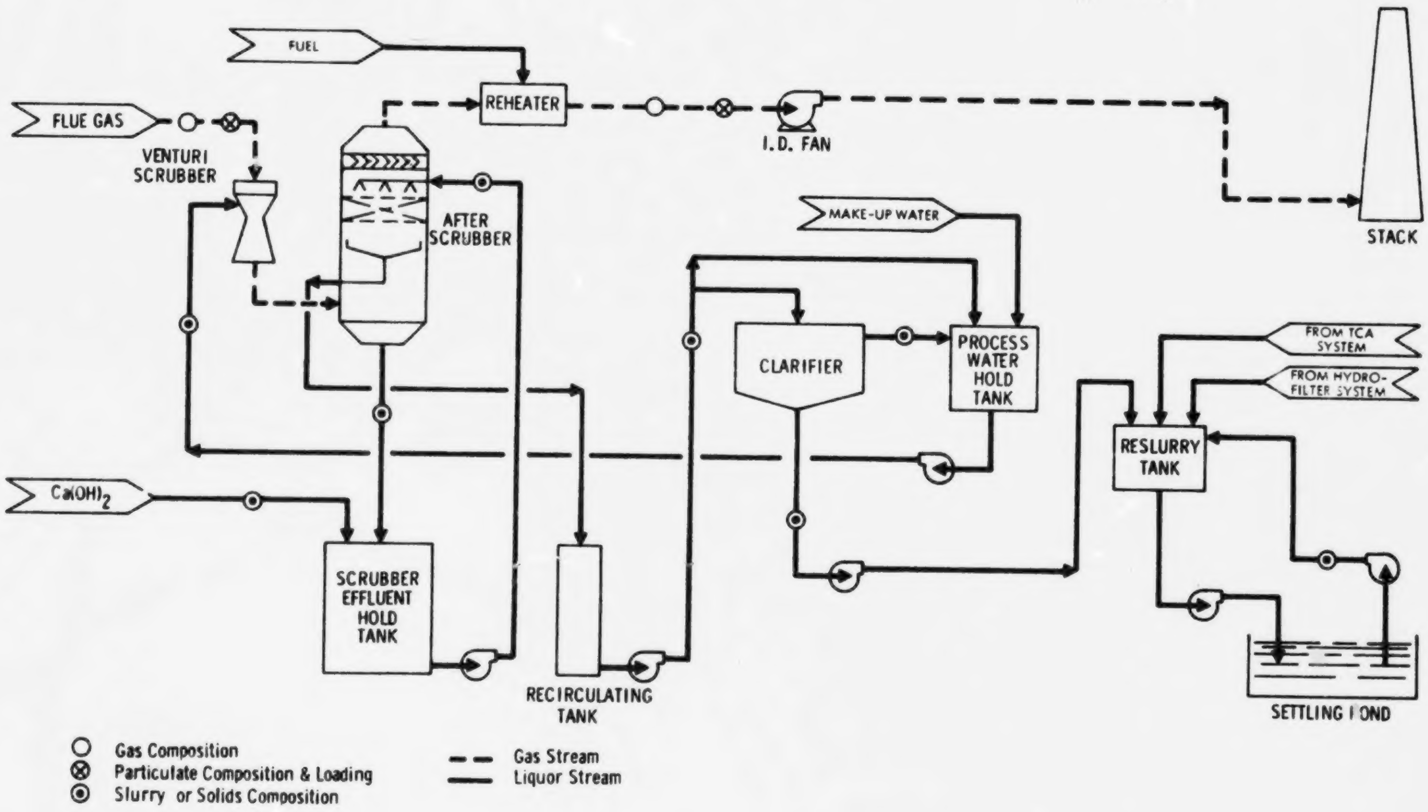


Figure 2

TYPICAL PROCESS FLOW DIAGRAM FOR TCA SYSTEM

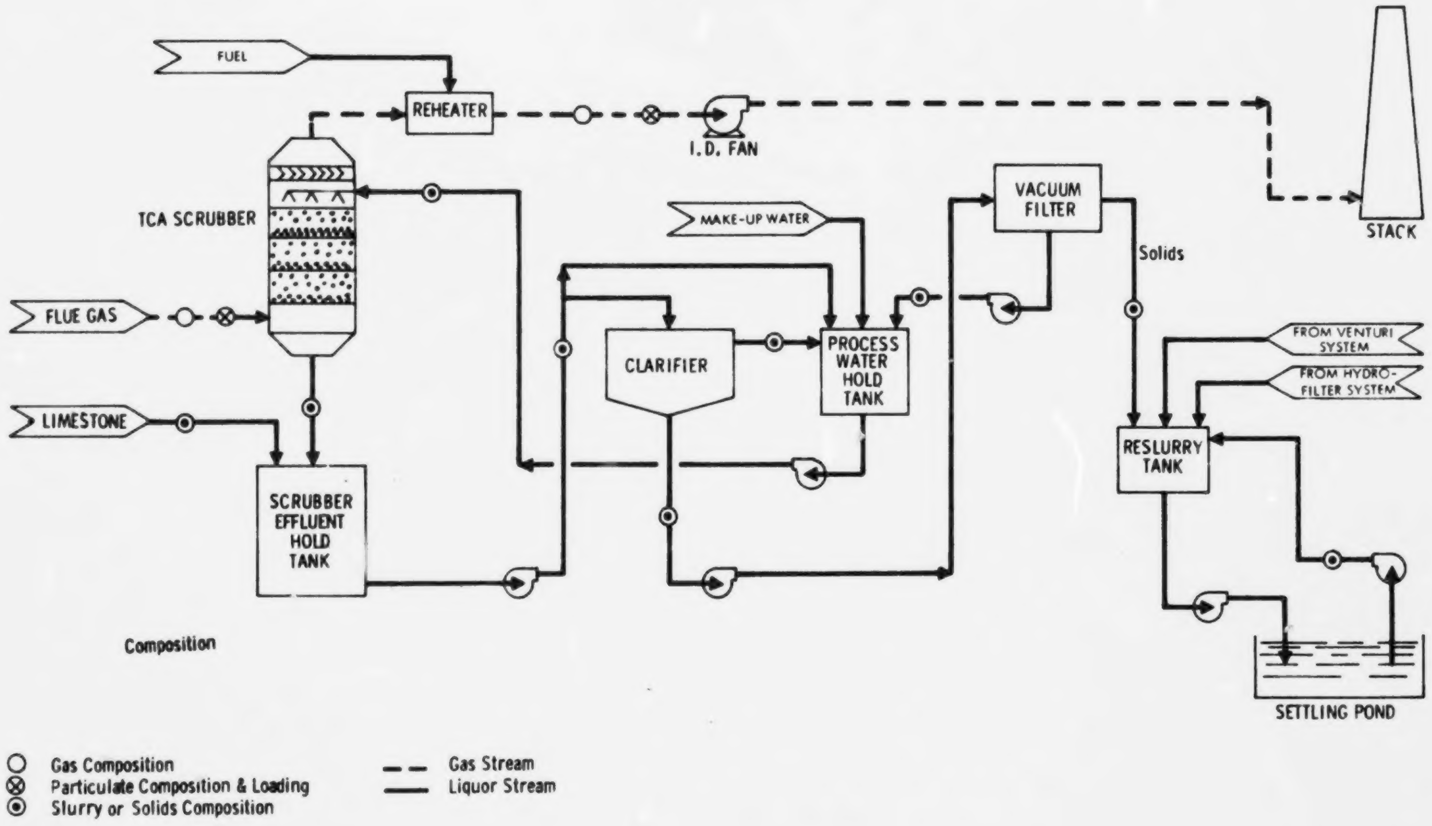
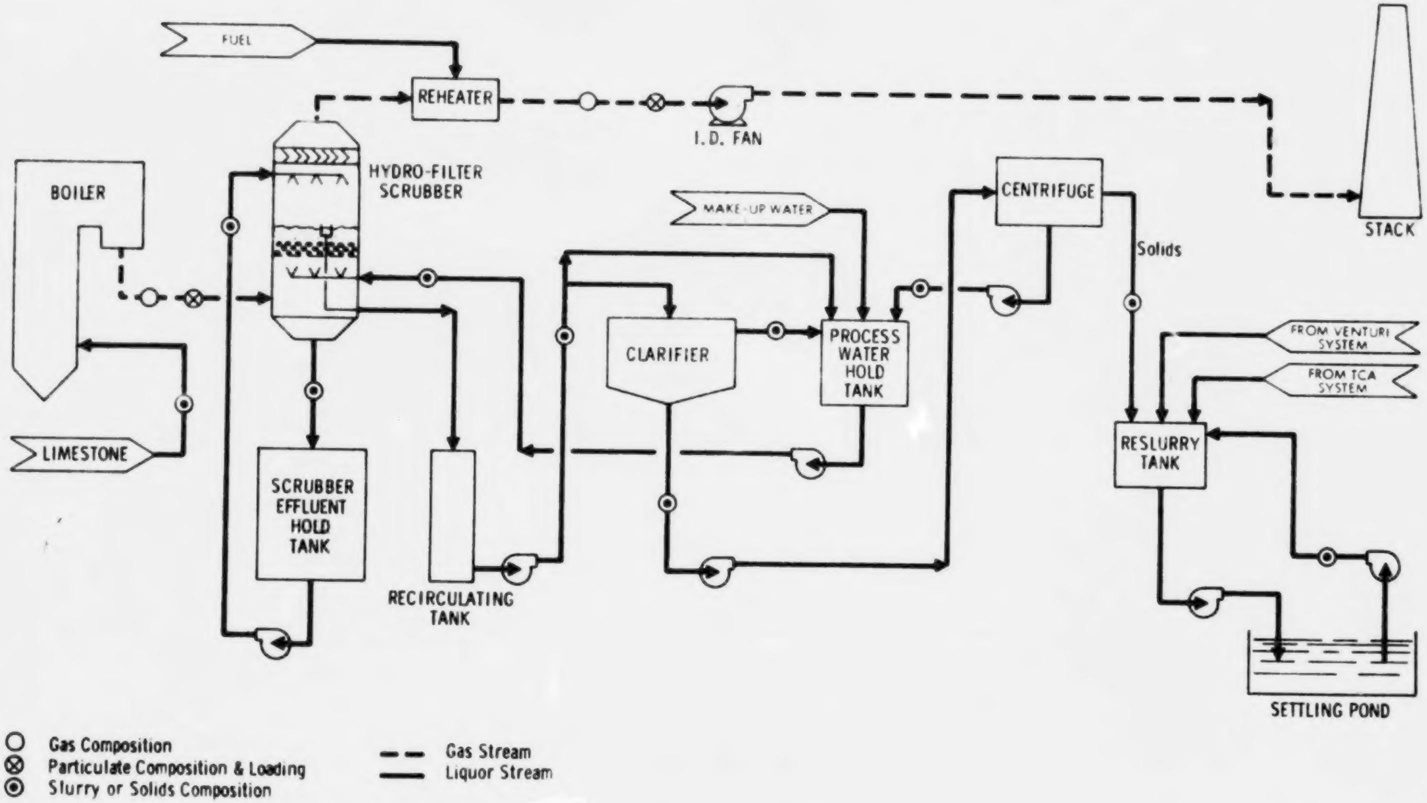


Figure 3

TYPICAL PROCESS FLOW DIAGRAM
FOR HYDRO-FILTER SYSTEM



Batch samples of coal, limestone, slurry and gas will be taken periodically during each test run for chemical analysis, particulate size sampling and limestone reactivity tests. The locations of these sample points are indicated shown on Figures 1, 2 and 3.

The Shawnee pilot facility contains five major areas: (1) the scrubber area (including tanks and pumps), (2) the operations building (including laboratory area, electrical gear, centrifuge and filter), (3) the thickener area (including pumps and tanks), (4) the utility area (including air compressors, air dryer, limestone storage silos, mix tanks, gravimetric-feeder, and pumps), and (5) the pond area. Figure 4 is a perspective sketch of the pilot facility. The pond area is shown at the extreme right; the three Clarifiers are near the center, adjacent to the operations building; and the scrubber area is in the foreground with the boiler facility to the left.

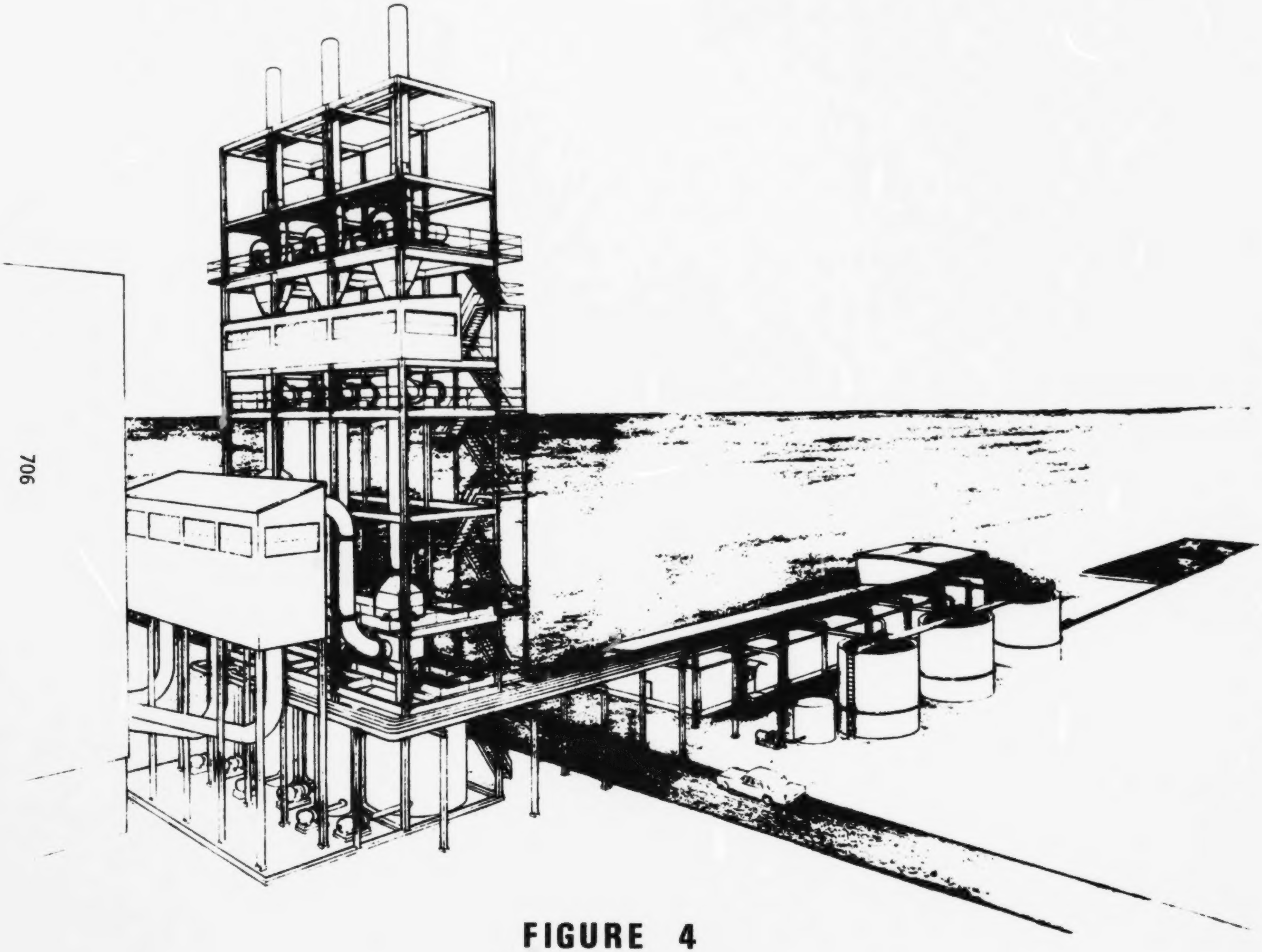


FIGURE 4
TEST FACILITY

TEST PROGRAM

DESIGN CONCEPTS

Data from the test program (Phase III) will be utilized to:

- Develop mathematical models for process and equipment scale-up to commercial (multi-hundred megawatt plant) scrubber systems.
- Evaluate the feasibility and long-term reliability of closed-loop limestone wet-scrubbing systems.

The following test periods have been defined:

(1) Air-Water Tests.

(2) Sodium Carbonate Scrubbing of Air-SO_2 Gas Mixtures.

(3) Break-In Testing for Wet-Scrubbing of Boiler Flue Gas with Limestone and Hydrate in the Scrubber Circuit and with Limestone and Dolomite in the Boiler.

(4) Screening Testing for Wet-Scrubbing of Boiler Flue Gas with Limestone and Hydrate in the Scrubber Circuit and with Limestone and Dolomite in the Boiler.

(5) Primary Testing for Wet-Scrubbing of Boiler Flue Gas with Limestone and Hydrate in the Scrubber Circuit and with Limestone and Dolomite in the Boiler.

Air-Water Tests. The experiments with air and water are designed to:

(1) Determine pressure drop model coefficients for all three scrubber systems without solids.

(2) Observe the fluid hydrodynamics within the scrubbers in a clean system, e.g. attempt to determine the droplet sizes in the venturi throat region.

(3) Determine the quantity of entrained liquid in gas leaving scrubber demister.

Sodium Carbonate Tests. In these tests, water solutions of sodium carbonate will be used to scrub SO_2 from mixtures of air and SO_2. The purpose of these tests is to determine uncertain model coefficients for gas-side controlling mass transfer for all three scrubber systems. These data may also be used to evaluate and design other systems which rely on sodium carbonate aqueous scrubbing.

Break-In Tests. The break-in test periods will be used to identify and resolve possible operating problems prior to initiation of screening testing. The primary objectives of the break-in tests are to:

(1) Determine scaling and plugging tendencies and evaluate various methods for scale removal. The limits of the levels of the most important scale-related variables which must be set during subsequent testing in order to prevent scaling will be identified, e.g. suspended solids concentration in scrubber inlet slurry, effluent hold tank residence time. An attempt will be made to develop reliable methods for detecting potentially deleterious scaling before complete pluggage or major scaling has occurred,

e.g. pressure drop information, liquor conductivity measurements, visual observation. Mechanical methods (chiseling, scraping) as well as chemical methods (muriatic acid, oxalic acid, soda ash) will be tested as means for removing scale.

(2) Determine solids separating and handling sapabilities. Various solids separating configurations will be evaluated for their effect upon settling characteristics, scaling tendencies, dewatering capability, reliability and the ability to approach steady state within the time constraints imposed during screening testing.

(3) Establish criteria for achievement of steady state conditions and ascertain the time required to achieve steady state for various operating changes.

(4) Determine the limitations of the system with respect to control of the independent variables over their required levels. Also, determine the replicability of dependent variable response to selected settings of independent variables.

(5) Evaluate the efficacy of the systems-data measurement capability.

(6) Supply information regarding the selection of levels of some of the less important independent variables which are to be held fixed during the screening testing. Also, evaluate selected combinations of scrubber/liquor piping flow configurations.

(7) Determine system reliability for subsequent screening and primary test requirements.

Screening Tests. The screening tests are designed to:

(1) Characterize, as completely as practicable, the effect of important independent variables on particulate removal and SO_2 removal for the three scrubber systems.

(2) Compare model predictions for pressure drop, particulate removal, and SO_2 removal with the data and determine the best-fit values for uncertain constants and coefficients within the models.

The screening tests are divided into two general categories:

(1) Factorial tests where the most important independent variables and selected "secondary" variables are treated in a fractional factorial test matrix.

(2) Sensitivity tests where less important variables are tested in an abbreviated test design.

A certain number of undefined tests will be allotted for the screening tests. This is to allow flexibility by permitting selection of further test runs influenced by results of prior factorial and sensitivity testing. Also, some of these runs can be used to replicate a previously tested set of conditions for a relatively long term test (1 - 2 weeks). This would allow preliminary verification on a longer term basis of potentially attractive operating modes, prior to the primary testing effort which is performed as the last portion of the test program.

Primary Tests. The objectives of the primary tests are to:

(1) Perform selected short-term testing to ascertain close-to-optimum operating conditions for each scrubber type and alkali injection mode.

(2) Perform long-term testing (two to four months) on the most attractive operating modes for each scrubber system to determine reliability of operation and to develop data for process economics and for scale-up to larger systems.

TEST SCHEDULE

The Break-In and screening testing will be divided into three blocks which are to be tested sequentially. They are:

(1) Block #1 - Limestone in Scrubber Circuit
(2) Block #2 - Hydrate in Scrubber Circuit
(3) Block #3 - Limestone in Boiler

The preliminary schedule for the test effort is presented in Figure 5. The estimated date for initiation of System Check-Out is March 1, 1972. The presented schedule should be considered approximate only, since it may not be feasible to adhere to a rigid schedule in a research and development program of this type.

Table 1 presents a description of the reports which are presently scheduled for general distribution.

TEST PROGRAM VARIABLES AND LEVELS

The levels of the independent variables for the air-water, sodium carbonate and screening experiments for all three scrubber systems are given in Tables 2 through 12*. The following conventions have been adopted in these tables (see Figures 1, 2, and 3):

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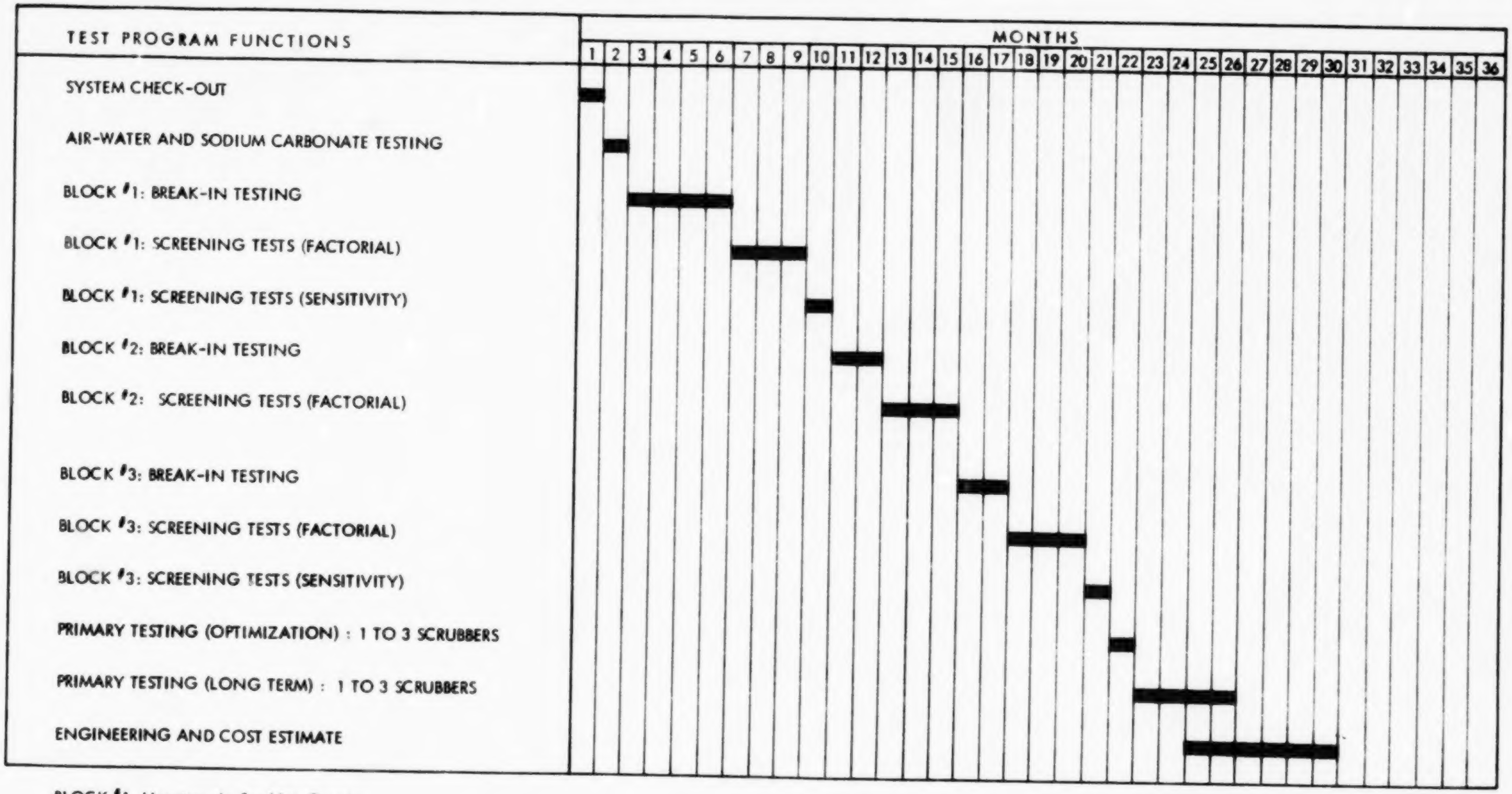
* These represent the levels of the statistically designed runs. A small number of runs in the test sequence have not been statistically designed.

FIGURE 5

PHASE III

SHAWNEE TEST SCHEDULE



BLOCK #1: Limestone in Scrubber Circuit

BLOCK #2: Hydrate in Scrubber Circuit

BLOCK #3: Limestone/Dolomite in Boiler

Table 1

TOPICAL AND FINAL REPORT DESCRIPTION

Report Title	Information to be Included	Estimated General Publication Date
1. Break-in Test Results for Block #1 - Limestone in Scrubber Circuit.	Summary of operational problems and resolutions, planned and actual test designs, results of air-water and Na_2CO_3 testing, utilization of data for model development, results of break-in testing with interpretation of data.	Two months after completion of Block #1 Break-in Tests
2. Screening Tests Results for Block #1 - Limestone in Scrubber Circuit.	Summary of operating problems and resolutions, planned and actual test designs, results of screening tests, interpretation of data, status of process model development.	Two to three months after completion of Block #1 Screening Tests
3. Break-in Screening Test Results for Block #2 - Hydrate in Scrubber Circuit	Summary of operational problems and resolutions, planned and actual test designs, results of break-in testing, results of screening testing, status of process model development, interpretation of data.	Two months after completion of Block #2 Screening Tests
4. Break-in and Screening Test Results for Block #3 - Limestone in Boiler.	Same as report #3 above	Two months after completion of Block #3 Screening Tests
5. Final Report	Summary of total test program with particular emphasis on: primary test results, mathematical models, scale-up design and economic studies.	Two months after completion of program

Table 2

Levels of Independent Variables for Air-Water Experiments

Venturi System		TCA System		Hydro-Filter System	
Variable	Levels	Variable	Levels	Variable	Levels
Scrubber configuration	1 Venturi & spray 2 Venturi & Pall-ring	Number of stages	1 1 stage 2 3	Air flow rate	1 10,000 cfm 2 20,000 3 30,000
Air flow rate	1 10,000 cfm 2 20,000 3 30,000	Air flow rate	1 10,000 cfm 2 20,000 3 30,000	Liquor flow rate-bottom sprays	1 0 gpm 2 100 3 200 4 400
Liquor flow rate-venturi	1 0 gpm 2 100 3 300 4 600	Liquor flow rate-top sprays	1 0 gpm 2 200 3 600 4 1200	Liquor flow rate-top sprays	1 0 gpm 2 100 3 200
Liquor flow rate-after-scrubber	1 0 gpm 2 300 3 600	Packing diameter	1 1 in. 2 1 1/2	Glass sphere diameter	1 5/8 in. 2 1
Plug position	1 25% open 2 50 3 75 4 100	Static height of packing	1 8 in. 2 12	Height of packing	1 3 in. 2 5
Demister	1 Centrifugal 2 Chevron			Overflow weir height above packing	1 0 in. 2 3 3 6

Table 3

Levels of Independent Variables for Sodium Carbonate Experiments

Venturi System		TCA System		Hydro-Filter System	
Variable	Levels	Variable	Levels	Variable	Levels
Scrubber configuration	1 Venturi alone 2 Pall-ring scrubber 3 Spray tower	Number of stages	1 1 stage 2 2	Air Flow rate	1 10,000 cfm 2 20,000 3 30,000
Air flow rate	1 10,000 cfm 2 15,000 3 20,000	Air flow rate	1 10,000 cfm 2 15,000 3 20,000	Liquor flow rate - bottom sprays	1 100 gpm 2 250 3 400
Liquor flow rate	1 100 gpm 2 250 3 400	Liquor flow rate - top sprays	1 200 gpm 2 500 3 800	Liquor flow rate - top sprays	1 0 gpm 2 100 3 200
Plug position	1 40% 2 60 3 80	Packing diameter	1 1 in. 2 1 1/2	Glass sphere diameter	1 5/8 2 1
		Static height of packing	1 6 in. 2 10 3 14	Height of packing	1 2 in. 2 3 3 5
				Overflow weir height above packing	1 0 in. 2 3 3 6

SO_2 concentration in air to be held at 600 ppm for all experiments.

Table 4

Levels of Independent Variables for Experiments
With Limestone in Scrubber Circuit: Venturi System

	Controllable Factors	Levels for Break-In (Group I)	Levels for Break-In (Group II)	Levels for Factorial Experiments	Levels for Sensitivity Experiments
Primary Variables	Scrubber configuration	Venturi & spray tower	Venturi & Pall-ring	1 Venturi & spray tower 2 Venturi & Pall-ring	Venturi & spray tower
	Stoichiometric ratio	1 1. 25 2 1. 50 3 1. 75 4 2. 00	1 1. 50 2 1. 75	1 1. 25 2 1. 75	1. 50
	Percent solids recirculated	1 4% 2 8 3 12 4 16	1 4% 2 10	1 8% 2 12	10%
	Gas flow rate	1 15, 000 cfm 2 30, 000	1 15, 000 cfm 2 30, 000	1 15, 000 cfm 2 30, 000	30, 000 cfm
	Liquor flow rate-venturi	300 gpm	300 gpm	1 300 gpm 2 600 gpm	300 gpm
	Liquor flow rate-after-scrubber	1 300 gpm 2 600	1 300 gpm 2 600	1 300 gpm 2 600	600 gpm
	E. H. T residence time	60 min.	60 min.	1 15 min. 2 60	60 min.
Secondary Variables	Flow configuration	14	1 14 2 15	1 14 2 15	14
	Plug position*	1 40% open 2 60 3 80 4 100	60% open	1 40% open 2 80	60% open
	Solids handling configuration	Clarifier/pond	Clarifier/pond	Clarifier/pond	1 Clarifier/pond 2 Clarifier/filter
	Limestone type	A	A	A	1 A 2 B
	Limestone particle size	90% through 300 mesh	90% through 300 mesh	1 90% through 300 mesh 2 90% through 200 mesh	90% through 300 mesh
	Limestone injection point*	E. H. T.	1 E. H. T. 2 P. W. H. T.	E. H. T.	E. H. T.
	Excess air	18%	18%	18%	1 18% 2 36
	Coal type	A	A	A	1 A 2 B
Variables Held Fixed	Saturation sprays	On	On	On	On
	Cooling of inlet liquor	No	No	No	No
	Coagulant	No	No	No	No

* These variables have been considered "primary variables" within the statistical designs for Break-In testing.

Table 5

Levels of Independent Variables for Experiments
With Limestone in Scrubber Circuit: TCA System

	Controllable Factors	Levels for Break-In (Group I)	Levels for Break-In (Group II)	Levels for Factorial Experiments	Levels for Sensitivity Experiments
Primary Variables	**Number of stages**	2 stages	2 stages	1 2 stages 2 3	3 stages
	Stoichiometric ratio	1 1.25 2 1.50 3 1.75 4 2.00	1 1.50 2 1.75	1 1.25 2 1.75	1.50
	Percent solids recirculated	1 4% 2 8 3 12 4 16	1 4% 2 10	1 8% 2 12	10%
	Gas flow rate	1 15,000 cfm 2 30,000	1 15,000 cfm 2 30,000	1 15,000 cfm 2 30,000	30,000 cfm
	Liquor flow rate-top sprays	1 600 gpm 2 1,200	1 600 gpm 2 1,200	1 600 gpm 2 1,200	1,200 gpm
	E.H.T. residence time	1 15 min. 2 60	60 min.	1 15 min. 2 60	60 min.
Secondary Variables	**Flow configuration** *	22	1 23 2 24	1 22 2 23	22
	Limestone type	A	A	A	1 A 2 B
	Limestone particle size	90% through 300 mesh	90% through 300 mesh	1 90% through 300 mesh 2 90% through 200 mesh	90% through 300 mesh
	Limestone injection point*	1 E.H.T. 2 P.W.H.T.	E.H.T.	1 E.H.T. 2 P.W.H.T.	E.H.T.
	Excess air	18%	18%	18%	1 18% 2 36
	Coal type	A	A	A	1 A 2 B
	Saturation sprays	On	On	On	1 On 2 Off
	Cooling of inlet liquor	No	No	No	1 Yes 2 No
Variables Held Fixed	**Solids handling configuration**	Clarifier/pond	Clarifier/pond	Clarifier/pond	Clarifier/pond
	Coagulant	No	No	No	No
	Packing diameter	1 1/2 in.	1 1/2 in.	1 1/2 in.	1 1/2 in.
	Static height of packing	10 in.	10 in.	10 in.	10 in.

* These variables have been considered "primary variables" within the statistical designs for Break-In testing.

Table 6

Levels of Independent Variables for Experiments With Limestone in Scrubber Circuit: Hydro-Filter System

	Controllable Factors	Levels for Break-In (Group I)	Levels for Break-In (Group II)	Levels for Factorial Experiments	Levels for Sensitivity Experiments
Primary Variables	Stoichiometric ratio	1 1.25 2 1.50 3 1.75 4 2.00	1.50	1 1.25 2 1.75	1.50
	Percent solids recirculated	1 4% 2 8 3 12 4 16	1 6% 2 10%	1 8% 2 12	10%
	Gas flow rate	15,000 cfm	30,000 cfm	1 15,000 cfm 2 30,000	30,000 cfm
	Liquor flow rate-bottom sprays	1 200 gpm 2 400	400 gpm	1 200 gpm 2 400	400 gpm
	E. H. T. residence time	1 15 min. 2 60	60 min.	1 15 min. 2 60	60 min.
	Overflow weir height above packing	6 in.	6 in.	1 4 in. 2 8	6 in.
Secondary Variables	Flow configuration *	1 32 2 33	32	1 32 2 33	32
	Solids handling configuration *	Clarifier/pond	1 Clarifier/pond 2 Clarifier/centrifuge 3 Clarifier/filter	Clarifier/pond	1 Clarifier/pond 2 Clarifier/centrifuge
	Limestone type	A	A	A	1 A 2 B
	Limestone particle size	90% through 300 mesh	90% through 300 mesh	1 90% through 300 mesh 2 90% through 200 mesh	90% through 300 mesh
	Excess air *	18%	1 18% 2 36%	18%	1 18% 2 36
	Coal type	A	A	A	1 A 2 B
	Saturation sprays	On	On	On	1 On 2 Off
	Cooling of inlet liquor *	1 Yes 2 No	No	No	No
	Coagulant *	No	1 Yes 2 No	No	No
	Liquor flow rate-top sprays	100 gpm	N.C.	1 100 gpm 2 200	N.C.
Variables Held Fixed	Limestone injection point	E. H. T.	E. H. T.	E. H. T.	E. H. T.
	Glass sphere diameter	5/8 in.	5/8 in.	5/8 in.	5/8 in.
	Height of packing	3 in.	3 in.	3 in.	3 in.

* These variables have been considered "primary variables" within the statistical designs for Break-In testing.

Table 7

Levels of Independent Variables for Experiments
With Hydrate in Scrubber Circuit: Venturi System

	Controllable Factors	Levels for Break-In		Levels for Factorial Experiments	
Primary Variables	Scrubber configuration		Venturi & spray tower	1	Venturi alone
				2	Venturi & spray tower
	Stoichiometric ratio	1	0.9	1	0.9
		2	1.1	2	1.3
		3	1.3		
		4	1.5		
	Percent solids recirculated	1	4%	1	8%
		2	8	2	12
		3	12		
		4	16		
	Gas flow rate	1	15,000 cfm	1	15,000 cfm
		2	30,000	2	30,000
	Liquor flow rate-venturi		300 gpm	1	300 gpm
				2	600
	Liquor flow rate-after-scrubber	1	300 gpm	1	300 gpm
		2	600	2	600
	E.H.T. residence time	1	15 min.	1	15 min.
		2	60	2	60
	Plug position	1	40% open	1	40% open
		2	80%	2	80%
Secondary Variables	Flow configuration		14	1	14
				2	15
Variables Held Fixed	Saturation sprays		On		On
	Hydrate injection point		E.H.T.		E.H.T.
	Cooling of inlet liquor		No		No
	Excess air		18%		18%
	Coal type		A		A
	Coagulant		No		No
	Solids handling configuration		Clarifier/pond		Clarifier/pond

Table 8

Levels of Independent Variables for Experiments
With Hydrate in Scrubber Circuit: TCA System

	Controllable Factors	Levels for Break-In		Levels for Factorial Experiments	
Primary Variables	Number of stages		2 stages	1 2	2 stages 3
	Stoichiometric ratio	1 2 3 4	0.9 1.1 1.3 1.5	1 2	0.9 1.3
	Percent solids recirculated	1 2 3 4	4% 8 12 16	1 2	8% 12
	Gas flow rate	1 2	15,000 cfm 30,000	1 2	15,000 cfm 30,000
	Liquor flow rate-top sprays	1 2	600 gpm 1,200	1 2	600 gpm 1,200
	E.H.T. residence time	1 2	15 min. 60	1 2	15 min. 60
Secondary Variables	Flow configuration*	1 2	22 23	1 2	22 23
Variables Held Fixed	Saturation sprays		On		On
	Static height of packing		10 in.		10 in.
	Solids handling configuration		Clarifier/pond		Clarifier/pond
	Hydrate injection point		E.H.T.		E.H.T.
	Cooling of inlet liquor		No		No
	Excess air		18%		18%
	Coal type		A		A
	Coagulant		No		No
	Packing diameter		1 1/2 in.		1 1/2 in.

* These variables have been considered "primary variables" within the statistical designs for Break-In testing.

Levels of Independent Variables for Experiments
With Hydrate in Scrubber Circuit: Hydro-Filter System

	Controllable Factors	Levels for Break-In		Levels for Factorial Experiments	
Primary Variables	Stoichiometric ratio	1 2 3 4	0.9 1.1 1.3 1.5	1 2	0.9 1.3
	Percent solids recirculated	1 2 3 4	4% 8 12 16	1 2	8% 12
	Gas flow rate	1 2	15,000 cfm 30,000	1 2	15,000 cfm 30,000
	Liquor flow rate-bottom sprays	1 2	200 gpm 400	1 2	200 gpm 400
	E.H.T. residence time	1 2	15 min. 60	1 2	15 min. 60
	Overflow weir height above packing		6 in.	1 2	4 in. 8
Secondary Variables	Flow configuration *	1 2	32 33	1 2	32 33
	Liquor flow rate-top sprays		100 gpm	1 2	100 gpm 200
Variables Held Fixed	**Saturation sprays**		On		On
	Cooling of inlet liquor		No		No
	Solids handling configuration		Clarifier/pond		Clarifier/pond
	Hydrate injection point		E.H.T.		E.H.T.
	Excess air		18%		18%
	Coal type		A		A
	Coagulant		No		No
	Glass sphere diameter		5/8 in.		5/8 in.
	Height of packing		3 in.		3 in.

*** These variables have been considered "primary variables" within the statistical designs for Break-In testing.**

Levels of Independent Variables for Experiments
With Alkali Additive in Boiler: Venturi System

	Controllable Factors	Levels for Break-In	Levels for Factorial Experiments	Levels for Sensitivity Experiments
Primary Variables	Stoichiometric ratio	1 1.25 2 1.50 3 1.75 4 2.00	1 1.25 2 1.75	1.50
	Percent solids recirculated	1 4% 2 8 3 12 4 16	1 8% 2 12	10%
	Gas flow rate	1 15,000 cfm 2 30,000	1 15,000 cfm 2 30,000	30,000 cfm
	Liquor flow rate-venturi	300 gpm	1 300 gpm 2 600	300 gpm
	Liquor flow rate-after-scrubber	1 300 gpm 2 600	1 300 gpm 2 600	600 gpm
	E.H.T. residence time	1 15 min. 2 60	1 15 min. 2 60	60 min.
	Boiler injection plane	A	1 A 2 B	A
Secondary Variables	Flow configuration	1 14 2 15	1 14 2 15	14
	Plug position *	60% open	1 40% open 2 80	60% open
	Solids handling configuration	Clarifier/pond	Clarifier/pond	1 Clarifier/pond 2 Clarifier/centrifuge
	Additive type	Limestone	Limestone	1 Limestone 2 Dolomite
	Additive particle size	90% through 300 mesh	1 90% through 300 mesh 2 90% through 200 mesh	90% through 300 mesh
	Excess air	18%	18%	1 18% 2 36
	Coal type	A	A	1 A 2 B
	Saturation sprays	On	On	1 On 2 Off
Variables Held Fixed	Cooling of inlet liquor	No	No	No
	Coagulant	No	No	No
	Scrubber configuration	Venturi & spray tower	Venturi & spray tower	Venturi & spray tower

* These variables have been considered "**primary variables**" within the statistical designs for Break-In testing.

Levels of Independent Variables for Experiments
With Alkali Additive in Boiler: TCA System

	Controllable Factors	Levels for Break-In	Levels for Factorial Experiments	Levels for Sensitivity Experiments
Primary Variables	Number of stages	2 stages	1 2 stages 2 3	3 stages
	Stoichiometric ratio	1 1.25 2 1.50 3 1.75 4 2.00	1 1.25 2 1.75	1.50
	Precent solids recirculated	1 4% 2 8 3 12 4 30	1 8% 2 12	10%
	Gas flow rate	1 15,000 cfm 2 30,000	1 15,000 cfm 2 30,000	30,000 cfm
	Liquor flow rate-top sprays	1 600 gpm 2 1200	1 600 gpm 2 1200	1200 gpm
	E.H.T. residence time	1 15 min. 2 60	1 15 min. 2 60	60 min.
	Boiler injection plane	A	1 A 2 B	A
Secondary Variables	Flow configuration*	1 22 2 23	1 22 2 23	22
	Solids handling configuration	Clarifier/pond	Clarifier/pond	1 Clarifier/pond 2 Clarifier/filter
	Additive type	Limestone	Limestone	1 Limestone 2 Dolomite
	Additive particle size	90% through 300 mesh	1 90% through 300 mesh 2 90% through 200 mesh	90% through 300 mesh
	Excess air	18%	18%	1 18% 2 36
	Coal type	A	A	1 A 2 B
Variables Held Fixed	Saturation sprays	On	On	On
	Cooling of inlet liquor	No	No	No
	Coagulant	No	No	No
	Packing diameter	1 1/2 in.	1 1/2 in.	1 1/2 in.
	Static height of packing	10 in.	10 in.	10 in.

* These variables have been considered "primary variables" within the statistical designs for Break-In testing.

Table 12

Levels of Independent Variables for Experiments With Alkali Additive in Boiler: Hydro-Filter System

	Controllable Factors	Levels for Break-In	Levels for Factorial Experiments	Levels for Sensitivity Experiments
Primary Variables	Stoichiometric ratio	1 1.25 2 1.50 3 1.75 4 2.00	1 1.25 2 1.75	**1.50**
	Percent solids recirculated	1 4% 2 8 3 12 4 16	1 8% 2 12	**10%**
	Gas flow rate	1 15,000 cfm 2 30,000	1 15,000 cfm 2 30,000	**30,000 cfm**
	Liquor flow rate-bottom sprays	1 200 gpm 2 400	1 200 gpm 2 400	**400 gpm**
	E.H.T. residence time	1 15 min. 2 60	1 15 min. 2 60	**60 min.**
	Overflow weir height above packing	6 in.	1 4 in. 2 8	**6 in.**
	Boiler injection plane	A	1 A 2 B	**A**
Secondary Variables	Flow configuration *	1 32 2 33	1 32 2 33	**32**
	Liquor flow rate-top sprays	100 gpm	1 100 gpm 2 200	**N.C.**
	Additive type	Limestone	Limestone	**1 Limestone** **2 Dolomite**
	Additive particle size	90% through 300 mesh	1 90% through 300 mesh 2 90% through 200 mesh	**90% through 300 mesh**
	Excess air	18%	18%	**1 18%** **2 36**
	Coal type	A	A	**1 A** **2 B**
	Saturation sprays	On	On	**1 On** **2 Off**
	Cooling of inlet liquor	No	No	**1 Yes** **2 No**
Variables Held Fixed	Solids handling configuration	Clarifier/pond	Clarifier/pond	**Clarifier/pond**
	Coagulant	No	No	No
	Glass sphere diameter	5/8 in.	5/8 in.	5/8 in.
	Height of packing	3 in.	3 in.	3 in.

* These variables have been considered "**primary variables**" within the statisti[illegible]

(1) Limestone type A and B refers to limestone from two different quarry sites.

(2) Coal type A and B refers to coal of two different sulfur concentrations, i.e. high and low sulfur coal.

(3) Boiler injection plane A and B refers to two different temperature regimes, for additive injection, within the boiler.

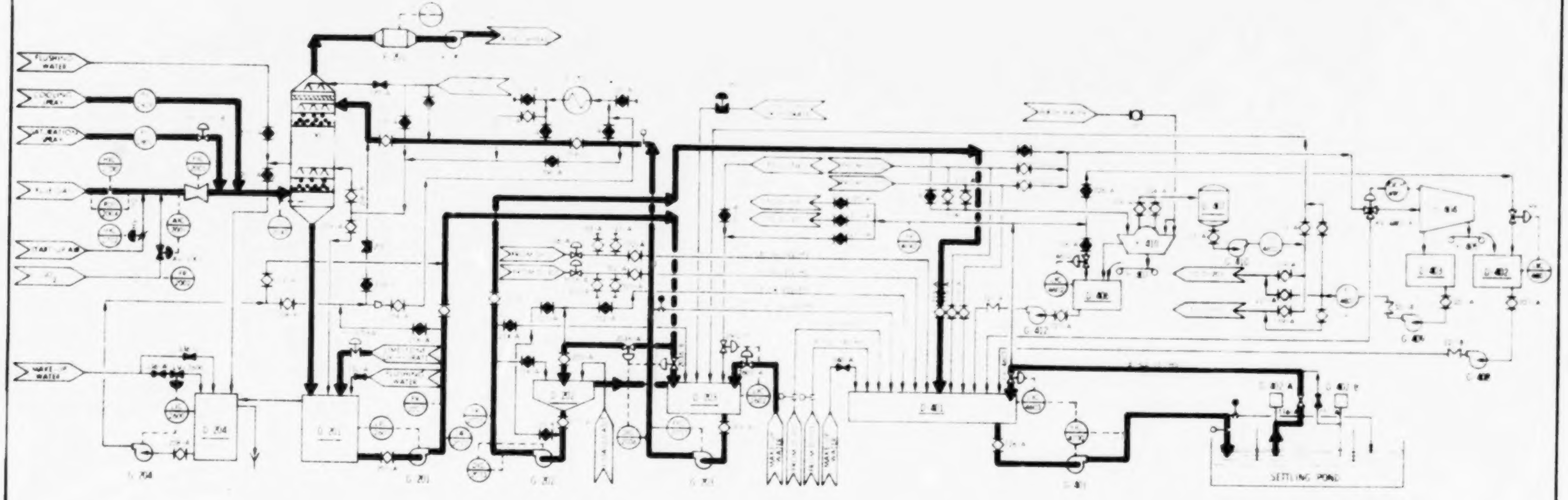
(4) E.H.T. and P.W.H.T. refer to the Effluent Hold Tank and the Process Water Hold Tank, respectively.

(5) N.C. refers to a variable which is "not controlled."

The flow configuration numbers refer to specific flow configurations for each scrubber system. As an example, the TCA flow configuration numbers 22 and 23 are shown in Figure 6 and 7, respectively.

Selection of Independent Variables

Generally, the independent variables chosen for a specific set of runs were those variables considered to have a major effect on the criterion (dependent) variables in question. These judgments were based on the limited existing pilot plant data and the results from mathematical models which predict criterion variables as a function of the independent variables (see Ref. 4). Also, the number of variables which can be tested within a set of runs is limited by the schedule time limitations and the desired statistical "resolutions" (see next section). For the break-in experiments, the dependent variables are SO_2 removal, particulate removal, plugging and scaling of critical pieces of equipment, solids separating capabilities (settling, etc.), length of time to reach "steady state" and system reliability.



EQUIPMENT LIST

VESSELS AND TANKS

C-201	TCA SCRUBBER
D-201	SCRUBBER EFFLUENT HOLD TANK
D-202	CLARIFIER
D-203	PROCESS WATER HOLD TANK
D-204	RECIRCULATING TANK
D-401	RESLURRY TANK
D-402	CENTRIFUGE SOLIDS RESLURRY TANK
D-403	CENTRATE RETURN SUMP
D-406	FILTER SOLIDS RESLURRY TANK
D-407	FILTER RECEIVER TANK

PUMPS

G-201	SCRUBBER EFFLUENT HOLD TANK PUMP
G-202	CLARIFIER UNDERFLOW PUMP
G-203	SCRUBBER PROCESS WATER RECIRCULATING PUMP
G-204	RECIRCULATING PUMP
G-401	[illegible] TRANSFER PUMP
G-412 A G-412 B	[illegible] WATER RETURN PUMPS
G-416	CENTRIFUGE SOLIDS RESLURRY PUMP
G-404	CENTRATE RETURN PUMP
[illegible]	FILTRATE RETURN PUMP
[illegible]	[illegible] SOLIDS RESLURRY [illegible]

MISCELLANEOUS EQUIPMENT

L-201	PROCESS LIQUOR COOLER
E-201	REHEATER
K-201	ID FAN
F-404	CLARIFIER UNDERFLOW CENTRIFUGE
L-405	CENTRIFUGE SOLIDS WEIGH SCALE
L-407	FILTER SOLIDS WEIGH SCALE
F-410	CLARIFIER UNDERFLOW VACUUM FILTER

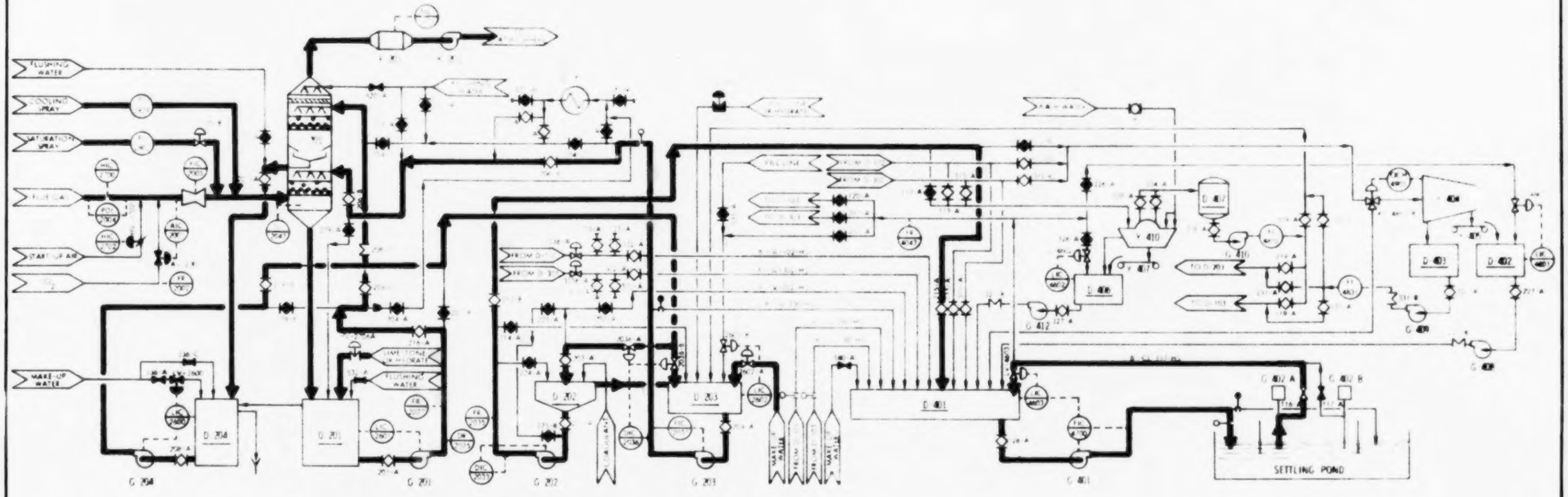
THE HEAVY SOLID LINES REPRESENT THE BASIC FLOW CONFIGURATION. ALTERNATE CONFIGURATIONS NOT REPRESENTED ARE:

- A FILTER OR CENTRIFUGE FOR SOLIDS HANDLING
- ALKALI ADDITION TO THE PROCESS WATER HOLD TANK
- SATURATION SPRAYS NOT IN USE
- A COOLER FOR SCRUBBER INLET LIQUOR
- A SINGLE OR TRIPLE STAGE TCA

FOR BOILER INJECTION OF ALKALI, THE CLACINED ALKALI ENTERS THE SYSTEM IN THE FLUE GAS

LEGEND —⊗— Valve Open —◆— Valve Closed

FIGURE 6
TCA SYSTEM
FLOW CONFIGURATION 22



EQUIPMENT LIST

VESSELS AND TANKS

C-201	TCA SCRUBBER
D-201	SCRUBBER EFFLUENT HOLD TANK
D-202	CLARIFIER
D-203	PROCESS WATER HOLD TANK
D-204	RECIRCULATING TANK
D-401	RESLURRY TANK
D-402	CENTRIFUGE SOLIDS RESLURRY TANK
D-403	CENTRATE RETURN SUMP
D-406	FILTER SOLIDS RESLURRY TANK
D-407	FILTER RECEIVER TANK

PUMPS

G-201	SCRUBBER EFFLUENT HOLD TANK PUMP
G-202	CLARIFIER UNDERFLOW PUMP
G-203	SCRUBBER PROCESS WATER RECIRCULATING PUMP
G-204	RECIRCULATING PUMP
G-401	SLURRY TRANSFER PUMP
G-402 A G-402 B	DECANTED WATER RETURN PUMPS
G-408	CENTRIFUGE SOLIDS RESLURRY PUMP
G-409	CENTRATE RETURN PUMP
G-410	FILTRATE RETURN PUMP
G-412	FILTER SOLIDS RESLURRY

MISCELLANEOUS EQUIPMENT

E-201	PROCESS LIQUOR COOLER
F-201	REHEATER
K-201	ID FAN
Y-404	CLARIFIER UNDERFLOW CENTRIFUGE
Y-405	CENTRIFUGE SOLIDS WEIGH SCALE
Y-407	FILTER SOLIDS WEIGH SCALE
Y-410	CLARIFIER UNDERFLOW VACUUM FILTER

THE HEAVY SOLID LINES REPRESENT THE BASIC FLOW CONFIGURATION. ALTERNATE CONFIGURATIONS NOT REPRESENTED ARE:

- A FILTER OR CENTRIFUGE FOR SOLIDS HANDLING
- ALKALI ADDITION TO THE PROCESS WATER HOLD TANK
- SATURATION SPRAYS NOT IN USE
- A COOLER FOR SCRUBBER INLET LIQUOR
- A SINGLE OR TRIPLE STAGE TCA

FOR BOILER INJECTION OF ALKALI, THE CALCINED ALKALI ENTERS THE SYSTEM IN THE FLUE GAS

FIGURE 7
TCA SYSTEM
FLOW CONFIGURATION 23

LEGEND: —◇— Valve Open —◆— Valve Closed

For break-in experiments with limestone in the scrubber circuit (Tables 4, 5 and 6), the designations of Group I and Group II refer to two different experimental sequences (designs), based upon different groupings of the variables to be investigated, e. g. in the venturi system, the limestone injection point is studied (varied) in Group II and not in Group I. All of the probable variables which may affect the criterion variables have been included in these designs (Group I and II). For example:

- The E. H. T. residence time (studied in Group I for TCA and Hydro-Filter) may affect the degree of supersaturation in the slurry system and, hence, influence scaling.
- Addition of coagulant (see Group II, Hydro-Filter) can affect clarifier settling characteristics and solids build-up within the system.
- Solids handling configurations (see Group II, Hydro-Filter) can affect solids separating (dewatering) and handling characteristics. Also, different configurations can affect reliability and the duration of the approach to steady-state after system upsets.
- Stoichiometric ratio and the percent solids recirculated can directly affect system plugging tendencies, clarifier settling characteristics, SO_2 removal and system overall chemistry.
- Excess air (studied in Group II, Hydro-Filter can affect the degree of oxidation of sulfite to sulfate and, hence, the system settling characteristics, scaling tendencies and SO_2 removal.
- Plug position (Group I, venturi) can affect SO_2 removal, particulate removal and scaling within the venturi.

For break-in tests with hydrate in the scrubber circuit and limestone/dolomite in the boiler, (Tables 7 through 12) the variables to be studied are fewer, since it is assumed that many of the operating problems will have been solved during testing with limestone in the scrubber circuit.

For the screening experiments, the criterion variables are SO_2 removal and particulate removal. The variables considered to have significant effects upon these dependent variables are shown in Tables 4 through 12. There are two types of variables considered in the screening experiments: (1) primary and (2) secondary variables. Primary variables are those considered to have a major effect upon the criterion variables while secondary variables are considered to have lesser, though significant effects. The screening experiments, as mentioned previously, are of two types:

(1) Factorial tests where the primary variables and "selected" secondary variables are treated in a fractional factorial test matrix.

(2) Sensitivity tests where the remainder of the secondary variables are tested in an abbreviated test design.

Selection of Levels for Independent Variables

The levels of the independent variables have been chosen using engineering judgment, pilot plant test results, the restraints of the system and results from mathematical models which relate the criterion and independent variables.

In many of the experimental sequences it was preferable to vary certain controllable factors over their maximum design ranges. For gas flow rate, the stable operating range is from about 10,000 to 30,000 cfm in each scrubber system. For liquor flow rates to the venturi and after-scrubbers, the controllable operating ranges are from about 100 to 600 gpm. For the Hydro-Filter bottom and top sprays, the allowable limits of liquor flow rates are from 100 to 600 gpm and 100 to 400 gpm, respectively. For liquor flow rates to the TCA, the controllable operating range is from about 200 to 1200 gpm.

As mentioned previously, two of the stated objectives for the break-in periods are: (1) to provide information regarding the limitations of the system with respect to control of the independent variables over their "desired" levels and (2) to define the limits of the levels of the important scale (or operating-problem) related variables. Therefore, severe (or unfavorable) operating ranges have been selected for a number of the independent variables, e.g. stoichiometric ratio and percent solids recirculated, during the break-in testing.

For the screening experiments, the variations in stoichiometric ratio from 1.25 to 1.75 and from 0.9 to 1.3 for limestone addition and hydrate addition, respectively, were based upon limited pilot plant data, which indicated reasonable SO_2 removals at these levels. The selected variation of percent solids recirculated from 8 to 12% was also based on limited data, which indicated that severe scaling or plugging would likely occur outside of these limits. Maximum ranges of gas rate variation (10,000 to 30,000 cfm) and liquid-to-gas ratio variation (about 10 to 60) were chosen in order to determine scale-up effects as accurately as possible. Obviously, the choices of the values of many of the variables listed in Table 4 through 12 may have to be modified once break-in testing has been completed.

STATISTICAL DESIGNS

The test sequences (presented in Ref. 5) are, generally, partial factorial designs based upon the chosen variables and levels and the restraints of time as outlined in Figure 5. For the screening (factorial) experiments, the statistical designs are partially replicated fractional-factorial sequences of Resolution IV* which have been selected with the understanding that an additional few experiments will be run, if necessary, in order to achieve Resolution V** designs for the significant variables. It is assumed, therefore, that the number of "significant" variables will actually be less than the number of primary variables listed in Tables 2 through 12.

TEST SCHEDULE

The total number of scheduled test runs are given in Table 13 and the estimated duration (line-out and "steady-state") of the runs in Table 14. The complete test schedule is presented in Ref. 6.

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* A Resolution IV design is a plan in which no main effect is confounded with any other main effect or two-factor interaction, but where two-factor interactions are confounded with one another.

** A Resolution V design is a plan in which no main effect or two-factor interaction is confounded with any other main effect or two-factor interaction but two factor interactions are confounded with three factor interactions.

Table 13

NUMBER OF SCHEDULED RUNS IN EPA TEST PROGRAM

Test Program Function	Number of Runs		
	Venturi	TCA	Hydro-Filter
Air-Water	20	20	20
Sodium Carbonate	24	20	20
Limestone in Scrubber (Block #1)			
Break-In	32	30	32
Factorial	40	32	32
Sensitivity	8	10	10
Undefined	8	8	8
Hydrate in Scrubber (Block #2)			
Break-In	16	16	16
Factorial	32	32	32
Undefined	8	8	8
Limestone in Boiler (Block #3)			
Break-In	19	19	19
Factorial	40	40	40
Sensitivity	10	10	10
Undefined	8	8	8
Primary Testing	To be defined		

Table 14

ESTIMATED TIME DURATION FOR SCHEDULED RUNS IN EPA TEST PROGRAM

Test Period	Block No.	Test Run Series Number (see Tables 47-56)	Estimated Time for Line-Out and Steady-State
Air-Water	-	101-120	1-2 hrs/run
Sodium Carbonate	-	201-224	2-6 hrs/run
Break-In	I	301-303	2-5 days/run
Break-In	I	401-416	2-3 days/run
Break-In	I	501-512	1-2 days/run
Break-In	I	601	5-8 days
Factorial	I	701-740	1-2 days/run
Sensitivity	I	801-810	2-3 days/run
Undefined	I	901-908[*]	1-2 days/run[*]
Break-In	II	1001-1016	1-2 days/run
Factorial	II	1101-1132	1-2 days/run
Undefined	II	1201-1208[*]	1-2 days/run[*]
Break-In	III	1301-1303	2-5 days/run
Break-In	III	1401-1416	2-3 days/run
Factorial	III	1501-1540	1-2 days/run
Sensitivity	III	1601-1610	1-2 days/run
Undefined	III	1701-1708[*]	1-2 days/run[*]

[*] May be fewer runs at longer durations each.

In Table 15, examples of TEST SCHEDULE SHEETS for TCA system factorial experiments with limestone in the scrubber circuit (Block #1) are presented. The second column refers to the "statistical design" table and run numbers, which have not been presented. Generally, the test design for all three scrubber systems must be "meshed," so that the scrubber systems can run simultaneously. Variables to be meshed (i.e., variables which are common to all scrubber systems) include limestone size, limestone type, and coal type. In addition, stoichiometric ratio must be meshed for runs where limestone is injected into the boiler (Block #3).

The same conventions used in Tables 2 through 12 have been used in Table 15.

ANALYTICAL SCHEDULE

Batch samples of coal, limestone slurry and gas will be taken periodically during each test run for chemical analyses, particulate size sampling and limestone reactivity tests. Locations of sample points have been shown on Figures 1, 2, and 3. In addition, clarifier settling tests, filter leaf tests, and filter and centrifuge "operational tests" will also be conducted periodically, during the break-in periods. A typical analytical schedule for break-in experiments with limestone in the scrubber circuit is shown in Table 16. Normally, there will be a separate analytical schedule sheet for each group or sub-group of tests.

Table 15

TEST SCHEDULE
FACTORIAL EXPERIMENTS FOR LIMESTONE IN SCRUBBER CIRCUIT: TCA SYSTEM

Run No.	Stat. Design		Flow Configuration	No. of Stages	Stoichiometric Ratio	Percent Solids Recirculated	Gas Flow Rate, cfm	Liquor Flow Rate, gpm	E.H.T. Residence Time, min.	Limestone Injection Point	Limestone Particle Size
	Table	Run									
701-2	25	1	23	2	1.25	8	15,000	1200	60	P.W.H.T.	90% through 300 mesh
702-2	↓	2	↓	↓	1.25	8	30,000	1200	15	P.W.H.T.	↓
703-2		11			1.75	12	30,000	600	60	E.H.T.	
704-2		12			1.75	12	15,000	600	15	E.H.T.	
705-2		7			1.75	8	15,000	600	60	P.W.H.T.	90% through 200 mesh
706-2		8			1.75	8	30,000	600	15	P.W.H.T.	↓
707-2		13			1.25	12	30,000	1200	60	E.H.T.	
708-2		14			1.25	12	15,000	1200	15	E.H.T.	
709-2		3	22		1.25	8	30,000	600	60	E.H.T.	90% through 300 mesh
710-2		4	↓		1.25	8	15,000	600	15	E.H.T.	↓
711-2		9			1.75	12	15,000	1200	60	P.W.H.T.	
712-2		10			1.75	12	30,000	1200	15	P.W.H.T.	
713-2		5			1.75	8	30,000	1200	60	E.H.T.	90% through 200 mesh
714-2		6			1.75	8	15,000	1200	15	E.H.T.	↓
715-2		15			1.25	12	15,000	600	60	P.W.H.T.	
716-2		16			1.25	12	30,000	600	15	P.W.H.T.	

Variables Held Constant	Value
Coal Type	A
Limestone Type	A
Packing Diameter	1-1/2 in.
Static Height of Packing	8 in.

Variables Held Constant	Value
Solids Handling Unit	Clarifier/Pond
Excess Air	18% (nominal)
Coagulant	No
Cooling of Inlet Liquor	No
Saturation Sprays	On

Table 15 (continued)

TEST SCHEDULE
FACTORIAL EXPERIMENTS FOR LIMESTONE IN
SCRUBBER CIRCUIT: TCA SYSTEM

Run No.	Stat. Design		Flow Configuration	No. of Stages	Stoichiometric Ratio	Percent Solids Recirculated	Gas Flow Rate, cfm	Liquor Flow Rate, gpm	E. H. T. Residence Time, min.	Limestone Injection Point	Limestone Particle Size
	Table	Run									
717-2	25	17	22	3	1.25	8	15,000	1200	60	E. H. T.	90% through 300 mesh
718-2		18					30,000	1200	15	E. H. T.	
719-2		19					30,000	600	60	P. W. H. T.	
720-2		20					15,000	600	15	P. W. H. T.	
721-2		21			1.75		30,000	1200	60	P. W. H. T.	90% through 200 mesh
722-2		22					15,000	1200	15	P. W. H. T.	
723-2		23					15,000	600	60	E. H. T.	
724-2		24					30,000	600	15	E. H. T.	
725-2		25				12	15,000	1200	60	E. H. T.	90% through 300 mesh
726-2		26					30,000	1200	15	E. H. T.	
727-2		27					30,000	600	60	P. W. H. T.	
728-2		28					15,000	600	15	P. W. H. T.	
729-2		29			1.25		30,000	1200	60	P. W. H. T.	90% through 200 mesh
730-2		30					15,000	1200	15	P. W. H. T.	
731-2		31					15,000	600	60	E. H. T.	
732-2		32					30,000	600	15	E. H. T.	

Variables Held Constant	Value
Coal Type	A
Limestone Type	A
Limestone Injection Point	E. H. T.
Packing Diameter	1-1/2 in.
Static Height of Packing	8 in.

Variables Held Constant	Value
Solids Handling Unit	Clarifier/Pond
Excess Air	18% (nominal)
Coagulant	No
Cooling of Inlet Liquor	No
Saturation Sprays	On

				LIQUID TESTS														SOLID TESTS																OTHER TESTS						
RUN NUMBER(S)	SYSTEM	[illegible]	SAMPLE POINT NO. (1)	Ca	Mg	Na	K	SO_3	SO_4	CO_3	NO_2	NO_3	Cl	TOTAL S	TOTAL N	pH	CONDUCTIVITY	$CaCO_3$	$MgCO_3$	$CaSO_4$	$Ca(OH)_2$	$Mg(OH)_2$	$CaSO_3$	$MgSO_3$	CaO	MgO	REACTIVITY (7)	SULFUR	HYDROGEN	TOTAL MOISTURE	ASH	SIZE (7)	GRAIN LOAD	% SOLIDS	SETTLING (8)	OPERATIONAL (8)	LEAF TEST (8)	TEST FREQUENCY DURING LINE-OUT PER RUN	TEST FREQUENCY DURING STEADY-STATE PER RUN	(9) AVERAGE TOTAL TESTS PER RUN
		SITE		MEQ/LITER										MG/LITER			(6)	GRAMS/LITER									-	WT %				μ	WT %							
401 to 416	COMMON	COAL																										X	X	X	X							(a)	-	-
		LIMESTONE	-															X	X						X	X	X											(a)	-	-
		HYDRATE	-																																					
		PARTICULATES, BOILER FLUE GAS	(2)																														X					(a)	-	-
		POND FEED	4814	X	X	X	X	X	X	X			X	X	X	X	X																	X				(b)	-	-
		POND RETURN LIQUID	(3)	X	X	X	X	X	X	X			X	X	X	X	X																	X				(b)	-	-
401-1 to 416-1	VENTURI	PARTICULATES, FLUE GAS FEED	1800, 1801																													X	X					(a)	-	-
		PARTICULATES, SCRUBBED GAS	1804																														X					(a)	-	-
		PARTICULATES, SCRUBBED GAS	1805																													X						(a)	-	-
		RECIRCULATING TANK INLET SLURRY	1823	X	X	X		X	X	X			X	X		X	X	X	X	X			X	X														(c)	1	23
		RECIRCULATING TANK OUTLET SLURRY	1815	X	X	X	X	X	X	X			X	X	X	X	X	X	X	X			X	X														(c)	1	25
		EFFLUENT HOLD TANK OUTLET SLURRY	1816	X	X	X		X	X	X			X	X		X	X	X	X	X			X												X			(c)	1	22
		PROCESS WATER HOLD TANK OUTLET SLURRY	1822	X	X	X	X	X	X	X			X	X	X	X	X	X	X	X			X	X														(c)	2	42
		PROCESS WATER HOLD TANK SLURRY	1819													X	X																					(c)	1	10
		AFTER-SCRUBBER OUTLET SLURRY (4)	1825	X	X	X	X	X	X				X	X		X	X	X	X	X			X															(c)	1	23
		AFTER-SCRUBBER OUTLET SLURRY (5)	1814													X	X																					-	1	2
		CLARIFIER UNDERFLOW	1818													X	X																	X				2	1	6
		CLARIFIER OVERFLOW	1828													X	X																	X				2	1	9
		FILTRATE RETURN LIQUOR	1820																																					
		CENTRATE RETURN LIQUOR	-																																					
		FILTER CAKE	-																																					
		CENTRIFUGE CAKE	-																																					
401-2 to 416-2	TCA	PARTICULATES, FLUE GAS FEED	2800, 2801																													X	X					(a)	-	-
		PARTICULATES, SCRUBBED GAS	2804																														X					(a)	-	-
		PARTICULATES, SCRUBBED GAS	2805																													X						(a)	-	-
		RECIRCULATING TANK INLET SLURRY	2823																																					
		RECIRCULATING TANK OUTLET SLURRY	2815																																					
		EFFLUENT HOLD TANK OUTLET SLURRY	2816	X	X	X	X	X	X	X			X	X	X	X	X	X	X	X			X	X											X			(c)	1	25
		PROCESS WATER HOLD TANK OUTLET SLURRY	2822	X	X	X	X	X	X	X			X	X	X	X	X	X	X	X			X	X														(c)	2	42
		PROCESS WATER HOLD TANK SLURRY	2819													X	X																					(c)	1	10
		TCA OUTLET SLURRY (4)	2825	X	X	X	X	X	X	X			X	X	X	X	X	X	X	X			X	X														(c)	1	25
		TCA OUTLET SLURRY (5)	2814													X	X																					-	1	2
		CLARIFIER UNDERFLOW	2818													X	X																	X				2	1	6
		CLARIFIER OVERFLOW	2829													X	X																	X				2	1	9
		FILTRATE RETURN LIQUOR	2820																																					
		CENTRATE RETURN LIQUOR																																						
		FILTER CAKE																																						
		CENTRIFUGE CAKE	-																																					
401-3 to 416-3	HYDRO-FILTER	PARTICULATES, FLUE GAS FEED	3800, 3801																													X	X					(a)	-	-
		PARTICULATES, SCRUBBED GAS	3804																														X					(a)	-	-
		PARTICULATES, SCRUBBED GAS	3805																													X						(a)	-	-
		OVERFLOW WEIR OUTLET SLURRY	3823	X	X	X		X	X	X			X	X		X	X	X	X	X			X	X														(c)	1	23
		RECIRCULATING TANK OUTLET SLURRY	3815	X	X	X	X	X	X	X			X	X	X	X	X	X	X	X			X	X											X			(c)	1	25
		SLAKING TANK OUTLET SLURRY	3816	X	X	X	X	X	X	X			X	X	X	X	X	X	X	X			X	X														(c)	1	25
		PROCESS WATER HOLD TANK OUTLET SLURRY	3822	X	X	X	X	X	X	X			X	X	X	X	X	X	X	X			X	X														(c)	2	42
		PROCESS WATER HOLD TANK SLURRY	3819													X	X																					(c)	1	10
		HYDRO-FILTER OUTLET SLURRY (4)	3825	X	X	X	X	X	X	X			X	X	X	X	X	X	X	X			X	X														(c)	1	25
		HYDRO-FILTER OUTLET SLURRY (5)	3814													X	X																					-	1	2
		CLARIFIER UNDERFLOW	3810													X	X																	X				2	1	6
		CLARIFIER OVERFLOW	3829													X	X																	X				2	1	9
		FILTRATE RETURN LIQUOR	3820																																					
		CENTRATE RETURN LIQUOR																																						
		FILTER CAKE																																						
		CENTRIFUGE CAKE																																						
																																							Total	457

NOTES

(1) SAMPLE POINT NUMBERS WILL BE FOUND ON P&ID'S M-111, M-112, M-113, M-114

(2) FLUE GAS FROM BOILER #10 DUCT, UPSTREAM OF AIR HEATER

(3) OBTAINED FROM POND WATER RETURN PUMP 8" DISCHARGE LINE

(4) LOCATED IN 36" SECTION OF SCRUBBER TAIL PIPE

(5) LOCATED IN 48" SECTION OF SCRUBBER TAIL PIPE

(6) UNITS OF MICRO-MHOS/CM

(7) TEST TO BE DETERMINED

(8) SEE APPENDIX A FOR DESCRIPTION OF TESTS

(a) One per two runs.
(b) One per five runs.
(c) Only pH & conductivity at a frequency of four per run.

Total length of time for a single run is assumed to be from 2-3 days. (See Table 14)

TABLE 16

SAMPLING AND ANALYTICAL SCHEDULE FOR BREAK-IN EXPERIMENTS WITH LIMESTONE IN SCRUBBER CIRCUIT

In order to meet the formidable slurry, coal, and alkali analytical requirements of the facility at reasonable costs, equipment has been selected that minimizes manpower. For example, an x-ray fluorescence unit has been purchased, which should allow for comprehensive slurry analyses with reasonable manpower requirements. A summary of batch analytical methods for determining important species in slurry, coal and alkali is presented in Table 17.

In the particulate sampling area, equipment will be available to measure mass loading in the scrubber inlets and outlets. If the results of an EPA sponsored program with McCrone Associates are successful, this data will be supplemented with particulate size distribution data obtained with a multi-cyclone device.

Equipment has been carefully selected for gas analyses. For SO_2 analysis, six "Du Pont" photometric analyzers will be utilized for continuous operation at all three scrubber inlets and outlets. For H_2O, CO_2, N_2, and O_2 determinations, two "Process Analyzer" gas chromatographs have been purchased for intermittent operation at each scrubber inlet and outlet as well as two "Environmetrics" NO_x analyzers. pH will be monitored on a continuous basis using fifteen "Universal Interlox" pH analyzers. Three "Universal Interlox" electrolytic analyzers will be used to monitor electrical conductivity.

Table 17

FIELD METHODS FOR BATCH CHEMICAL ANALYSIS OF SLURRY, COAL AND ALKALI SAMPLES

Species Desired	Field Method
Sodium	Atomic Absorption
Potassium Calcium Magnesium Choride Total Sulfur	X-Ray Fluorescence
Total Sulfite and Bi-Sulfite	Dead Stop Iodometric
Total Carbonate and Bi-Carbonate	Infrared Analyser
Nitrite Nitrate	Ultra-Violet Technique

DATA ACQUISITION

Over 150 pieces of data (flow rates, temperatures, pH's etc.) are to be recorded automatically and continuously onto magnetic tape at the pilot plant site. At Bechtel Corporation, in San Francisco, all field process data (including results of analytical analyses and manually recorded information) will be placed into a "random access" computer file. The data will then be printed and plotted in suitable formats for distribution and assessment by Bechtel, EPA, and TVA personnel. A computer program will average data during the "Steady-state" run sequences, identify possible erroneous data points, etc. Another program will "adjust" data which are functions of temperature and/or pressure and convert certain data to more useful units.

DATA ANALYSIS

Statistical computer programs will analyse the data to determine, for the major dependent variable (SO_2 removal), the magnitude of the main effects and the two-factor interactions for all the major independent variables, as well as the magnitude of time trends, systematic upsets, and random error.

Model predictions for the dependent variables of pressure drop, particulate removal, and SO_2 removal (see Ref. 4) will be compared with the data and the "best-fit" values for uncertain constants and coefficients within the models calculated. For pressure drop and particulate removal, the form of the proposed models can also be checked. All models will be modified, if necessary, for better fit to the data.

SUMMARY

The Office of Air Programs (OAP) of the Environmental Protection Agency (EPA) has sponsored a program to fully characterize wet limestone scrubbing for removal of sulfur dioxide and particulates from boiler flue gas. Thes test facility consists of three parallel scrubber systems, each capable of treating approximately 30,000 acfm of flue gas, which are integrated into the flue gas ductwork of an existing coal-fired boiler at the TVA Shawnee Power Station, Paducah, Kentucky. Construction at the TVA power station is approximately 80 percent complete, with start-up presently scheduled for March, 1972.

Bechtel Corporation, as the major contractor, has prepared the detailed design of the test facility, is developing the test program and will direct the test efforts. TVA is constructing the facility and will operate the unit during the test program, which is scheduled to last 30 months.

Three basic test periods have been defined:

(1) Break-In Tests
(2) Screening Tests
(3) Primary Tests

"Break-in" testing will ascertain operational problems and variable control limitations and establish some attractive operating configurations.

"Screening" testing will define the influence of process independent variables on the dependent (performance) variables. Results from these tests will be used to perfect the mathematical models, which will then be valid for optimization and commercial scale-up.

Primary testing will be used to ascertain conditions for maximum performance of the scrubber systems and to demonstrate long-term process economics and reliability.

REFERENCES

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ECONOMICS OF LIMESTONE WET SCRUBBING SYSTEM

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Prepared for
Second International Lime/Limestone
Wet Scrubbing Symposium
New Orleans, Louisiana
November 8-12, 1971

ECONOMICS OF LIMESTONE WET SCRUBBING SYSTEM

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ABSTRACT

This paper describes factors influencing the costs of full-scale limestone scrubbing installations. Data on capital costs are presented, together with process and mechanical design criteria which most greatly affect these costs. Among the latter are corrosivity, erosion, scaling, local site factors, environmental impact, weatherizing, front and back end logistics, retrofit limitations, operating control philosophy. A case history is cited for an eastern utility planning retrofit scrubbers on a multiple-boiler installation. Operating costs are broken down into their components, and a range for each of these is given. The importance of these cost considerations in planning programs for compliance is examined.

* Prepared for presentation at the International Symposium for Wet Limestone Scrubbing, Nov. 8-12, 1971, New Orleans, Louisiana

INTRODUCTION AND BACKGROUND

The Environmental Protection Agency, acting in accordance with the mandates of the 1970 Clean Air Act, has set in motion the regulatory mechanism to achieve primary ambient standards of air quality within 3 years following June,1972. The states are busy preparing their programs for implementing this time table, and these are to be submitted to EPA by February, 1972. Many of the major urban areas have already enacted portions of these plans into local regulations which must be complied with by June, 1975.

Major operators of stationary combustion equipment are concerned with the effects of this activity on their overall operations. Not only are major capital outlays indicated, over and above those traditionally associated with fossil fuel equipment, but extra operating costs as well. Those of us who are following the progress of stack gas cleanup the closest would be less than frank if we did not recognize that these costs are exceeding estimates made during the early, conceptual stages of this program. Nevertheless, we should keep one thing in mind: the same factors contributing to spiraling costs here are to some degree at work in the other avenues available for emission control. While of scant comfort to a major utility, this should be somewhat reassuring to the engineer charged with finding the lowest-cost means of compliance. The recognition of what these cost components are, furthermore, provides a basis for challenge, comparison, and evaluation of progress being made elsewhere in the whole spectrum of pollution-control technology.

Early this year a major eastern utility retained Bechtel Corporation to prepare a study and estimate of fuel-burning alternates for one of its major existing facilities. Involved in the picture were four identical 180 Mw pulverized coal boilers burning 3-1/2% sulfur coal. Because of scheduled availability only one unit could be converted at a time, and it was necessary to make the conversion over a three-year period, in time for EPA deadlines.

The company was confronted with a number of possibilities, including (a) high-sulfur coal with both particulate and SO_2 scrubbing, as well as, (b) low-sulfur coal with particulate scrubbing only. The existing equipment was laid out in a typically close-coupled configuration, raising many questions of ducting, fan placement, and tandem vs. booster staging of fans. The capital costs for these two alternates are shown in Exhibits I and II (slide). It will be noted that a system for particulate removal only involved about 60% of the outlay of a system for particulate and SO_2 together, using rear-end limestone addition.

The following factors helped contribute in a major way to the capital cost of this facility, and these should be particularly noted by anyone who leans on generalized cost concepts, such as the convenient (but undependable) "0.6 factor" approach for SO_2 removal in power plants.

Raw Material Handling. Limestone was delivered by barge 9 months out of the year. This required a totally new conveying system, dedication of area for stockpiling, apart from the coal pile, and displacement of existing secondary service facilities. Supply logistics dictated a relatively high investment of this type to provide maximum long-term limestone economy and reliability of supply. Conveyors were sized for high-speed discharge rates to minimize conflicts in scheduling with coal barge deliveries. High reclaiming rates with large 24-hour silos were indicated to minimize the use of non-day shift labor.

Under conditions of delivery by truck, this portion of the investment could have been lower by $2/kw.

Limestone Milling. A complete, integrated milling operation was planned. The delivery of pulverized limestone by pipeline or truck from a central milling point would have lowered costs. However, the feasibility of such an operation was felt to be conjectural without a more extensive study.

Should future study demonstrate the practicality of off-site milling, the investment in both milling and raw stone handling could be transferred to a second party.

Scrubbing System. The scrubbing system is the heart of the operation and incurs the major cost burden, being 60-65% of the total investment. Some of the design-cost factors which have confronted system designers are listed below:

(1) Should a booster fan be added in series with existing fan, or should a completely new fan be specified?

(2) Should "pusher" fans be used, at the risk of eroding the fan blades, or should induced-draft fans be employed, with the possibility of high dewpoint corrosion and imbalancing?

(3) What corrosion mechanism is most likely, and what material is most suitable for fan blades following the scrubber? Stainless steel is costly and may be susceptible to stress corrosion. Peripheral speed considerations limit the use of

rubber-lined rotors. Certain alloys of interest, such as Corten, cannot be welded with safety. Deposits of slurry may build up excessive unbalanced forces on the fan blades, requiring periodic washing. Can washing be done on the line?

(4) Are reheat temperatures dictated by plume-drop considerations, (minimal reheat) or by dew-point corrosion factors (maximum reheat)? Is the existing stack properly lined with impervious insulating material so as to accept a flue gas with dewpoint characteristics?

(5) What is the most economical and lowest maintenance method of reheat —direct injection of combustion gas, or steam coils?

(6) What is the most suitable corrosion-resistant medium for field fabrication and assembly? For example, a shop-applied soft rubber lining appears to be the ideal protection for bisulfite slurry environments. (Field-applied rubber linings are generally more costly and less reliable than those applied under shop conditions.) For large vessels, however, there is no choice but field fabrication (of the steel), which means field application of the coating. Under such circumstances the cost of rubber linings is hard to justify.

(7) How far can one go in achieving economy of scale? For present scrubbers, the size limit for a single train is thought to be about 400, 000 cfm. There are a number of reasons for this, including non-uniform gas distribution problems (e. g. , if scrubbers are bigger, inlet ducts must be bigger) and the limited availability of matching fan capacity.

The size of I. D. fans will be physically limited by the maximum flow and pressure drop of the largest boiler units now being designed.

For ball mills, there is almost no limit, although at throughputs above 100 tons per hour (enough for 1000 Mw), there is greater concern for reliability. With skilled maintenance, bearing and liner repairs can normally be taken care of within 48 hours.

(8) What should the philosophy be in terms of providing standby pumps, mills, and scrubbers? For example, one major installation includes seven large circulating pumps, although the theoretical number needed is only four. Proposed EPA standards for new sources do not permit loss of control (i. e., as stated in the allowable 2-hour limit) more than once a year. This is a serious and costly constraint in terms of capital investment.

(9) Does damper design need to be positive shut-off, and if so, is double-dampering a reliable answer? Double dampers with intermediate air purging are preferred by some, whereas others insist upon a heavy crane-supported gate.

(10) To what extent is winterizing necessary? Here is an installation without winterizing (slide) and here is the same installation with enclosure (slide). Closing in of the equipment reduces exposure to freezing in small lines during down periods and also provides greater comfort during unscheduled maintenance. It may also encourage closer attention to the equipment, a matter of paramount interest during the early stages of equipment start-up.

(11) What type of instrumentation is most likely to satisfy conditions of power plant reliability? What are the response characteristics of fan-damper combinations under conditions requiring emergency by-pass? During such a period the operator must isolate 30 inches pressure drop out of a system total of 40 inches or more without pressurizing the boiler. This problem relates directly to the aforementioned question of maximum sizing for fans. If you are using a booster fan in series with an existing I. D. fan on a retrofit job, the problem may be compounded.

(12) What method of solids thickening is to be used? Does it stop at a pumpable consistency, or must filtration be employed? Can hydroclones or centrifuges be used without fear of slimes build-up? Are clarifiers the only safe answer? So far we have encountered no proposals which stop short of complete ponding or clarification.

All the foregoing considerations were realistically evaluated and taken into account in the aforementioned study. The results were neither excessively conservative nor overly optimistic. For instance, a successful working design throughout was anticipated as a matter of fact, despite the total lack of operational experience. On the other hand, reasonably generous sparing was provided.

Solids Handling. One of the more difficult aspects of limestone scrubbing is how to handle the waste solids. As typical wet filter cake, these account for approximately 40% of the coal tonnages. The rheological properties of these materials have proven to be somewhat unpredictable. In a scrubbing system where the alkali efficiency is low, virgin limestone comes through unaltered, a relatively high degree of dewatering will occur, the density and solids content will be high, but the cake may still slump. At higher efficiencies dewatering is incomplete, the density and solids content drop; on the other hand, the cake may retain its stiffness. How to stockpile, reload, and transport this material is a major challenge. Liquidity and plasticity of the filter cake are important criteria for design of such systems, and are variant.

For the plant in question, ponding was conceived as the best method for disposal —at a point four miles distant. (An alternate consideration involved total dewatering, followed by day-time reloading, and truck disposal.) Rubber-lined pipe delivered underflow from a battery of liquid cyclone thickeners out to the pond, and carbon steel pipe delivered the pond effluent back to the process.

One of the major cost elements here was a decision to provide all of the diking required for the life of the pond in advance, rather than in small increments involving a greater earthmoving total over the long haul. The argument here is manifested in a discount cash flow (DCF) trade-off of operating costs vs. capital costs. The capital costs shown in Exhibit I could be substantially reduced at the expense of increased operating costs in subsequent years. Diking, incidentally, accounted for $3.40 per kilowatt, or about 35% of the total solids disposal costs.

In summary, we have so far described a retrofit conversion job which would cost $43 per kw if done all at once. Since that is impossible, it is necessary to add escalation factors. These bring the cost to approximately $50/kw.

A large-scale modern installation would hope to achieve economies of layout, scale, and logistical planning such as to reduce all elements appreciably.

OPERATING COSTS

It is important to note the overwhelming effect which capital investment has upon operating costs. Exhibit III shows what may be expected for operating costs of limestone scrubbing across a wide range of power plant sizes (slide). (This data is typical only, and does not represent information from operating records or projections of Bechtel clients.) These are shown in terms of cost per ton of coal, as these are the units in which operations people think. Costs are divided into two categories —those which are a constant expense burden, regardless of load factor, and those which vary with the amount of fuel burned.

Capital charges account for about 95% of the non-varying costs. As percent of investment they may range from 12 to 15%. We have assumed a figure of 14%. Financial and accounting people might object to calling this a non-varying cost. It is really an average cost, made non-variant by a process of amortization. A typical exercise showing how such a figure is developed has been presented by H. W. Elder in a previous paper (1).

Prediction of maintenance costs is always a tricky business, since these are traditionally developed from operating experience. It must be remembered that such experience cannot yet be brought to bear on this type of installation. Chemical plants typically allow for a percentage of investment ranging from less than 2% to over 4%. A more rational approach is the "investment-year" basis (2), a typical example of which is shown in Exhibit V (slide). If the experience of SO_2 scrubbers proves equal to coke plants, for example, one might approach 2% maintenance after the fifth year. For the purposes shown we have been cautiously optimistic in assuming a figure of this magnitude. This compares with a rate of 1.4 to 1.7% for many power plants today.

The number of operators required, while low, depends on the size and number of units and upon considerations of retrofit vs. advance-planning.

We have not attempted to assess non-varying costs on a "per ton of coal" basis, as these change too much with size and capital investment. However, for each individual case one can approximate a unit cost, which will be somewhere in the range shown.

Among the variable costs, the largest unit item, next to limestone, may be waste disposal if trucking is considered. This is not included in Exhibits III and IV because the station has access to ponding. As previously noted, the cost of amortized pond preparation ends up instead in the capital charge account.

Power is a significant item for high-energy scrubbers —approximately 4% of boiler capability. The cost of reheat may require 2-1/2% of steam capability, unless the plant resorts to direct oil-or-gas fired injection. In this case station efficiency is not affected, but fuels more costly than coal are required. There are other potential maintenance and operating advantages to this type of reheat —for example, freedom from tube scaling. The ultimate trade-off still remains to be seen. We have yet to encounter a regenerative reheat system, although the economics are claimed to be favorable.

We have seen that the capital costs of scrubbing for particulate removal only run about 40% less than scrubbing for both SO_2 and particulate removal. Exhibit IV (slide) shows what the combined effect of altered technology and reduced investment does to operating costs. This demonstrates that the reduction in operating costs for particulate removal only is likewise about 40%.

COMBINATION OF PRECIPITATORS FOR PARTICULATE REMOVAL WITH SCRUBBERS FOR SO_2 REMOVAL

A frequently-asked question is: "Are there cost advantages to an electrostatic using a precipitator for particulate removal, followed by a wet scrubber for SO_2?" Some of the disadvantages are:

- an excessive space requirement, particularly in retrofit installations;
- the need for two separate waste handling systems.

On the other hand, there may be some advantages, such as:

- a reduction in capital cost (compared with 2-stage, all-wet scrubbing);
- an improvement in handling characteristics of waste solids, obtainable by blending of the lime solids filter cake with the precipitator fly ash.

From what we have just seen, if we were to leave off the second stage, i.e., omit SO_2 scrubbing, we would achieve about 40% reduction in costs. Looking at it in reverse, omission of the first stage and retention of the second might realize a cost reduction of $10-20 per kw which could be applied toward an investment in precipitators. This does not automatically establish a preference for 1st-stage electrostatic precipitators. On the other hand, the deliberate collection of dry fly ash for blending with filter cake may offer important savings in material handling costs. Exhibit VI (slide) shows the approximate relationship between limestone efficiency and the degree of mechanical moisture typically encountered in a filter cake. The greater the limestone efficiency, the higher the moisture content to be trucked away. As previously noted, this material may be much more manageable in terms of stiffness, low plasticity, etc., than one of lower water (but higher limestone) content. The handling problem can be eased somewhat by blending dry solids with wet filter cake, but its feasibility depends entirely on local circumstances.

OPPORTUNITIES FOR COST REDUCTION

There is great interest in knowing how truly representative these costs will be for other situations, particularly for new, large-scale fossil plants at the 500 Mw level and higher. We are making no claims on this score, as we believe each situation must be considered unto itself. It is, however, only being realistic to limit the installation of first-generation scrubbers to retrofit situations. These are at a distinct disadvantage in terms of: economics of scale, cramped hind quarters, and protracted construction schedules.

The following criteria deserve continuing investigation, as they would appear to offer the biggest opportunities for cost reductions. Detailed study is already underway in many quarters on these possibilities:

- Limestone mills - With good logistics and economics of scale, large modern power plants should not require more than one, or at most, two mills for their entire supply.
- Use of lime - If scaling problems can be solved, the potentially greater efficiencies associated with lime will reduce the tonnages of raw material and waste solids. This could open the door to over-the-fence supply economics and do away with milling requirements altogether.
- Elimination of clarifier - Some day, when process constraints have been more fully appraised, it may be found possible to by-pass the clarifier. This was proposed many years ago by ICI-Howden, but the conditions for its success have not been fully demonstrated.
- Plant layout - Progress in reduction of cost by appropriate planning offers hope for appreciable savings. Structural work and duct fabrication are major cost components so affected.
- Pond management - Much remains to be done on the flow classification properties of the various process slurries obtainable under different conditions before ponding practices are optimized. These findings will help dictate future operating practice. There is precedent in the ore beneficiation field, where the management of pond tailings has been developed into a fine art.

REFERENCES

(1) "Economics of Limestone - Wet Scrubbing"; Elder, H. W., International Symposium on Lime/Limestone Scrubbing for SO_2 Control, NAPCA, Pensacola, Florida, March 1970.

(2) "Predicting Maintenance Costs"; Chem. Eng., July 13, 1959.

EXHIBIT I

LIMESTONE SCRUBBING FOR MULTI-UNIT RETROFIT OVER A THREE-YEAR PERIOD

		PER KW	
		1971 COST	COST WITH PRORATED ADDITIONS*
1.	Limestone Unload, Storage, Reclaim	1.66	2.00
2.	Limestone Milling	4.02	4.90
3.	Scrubbing System	27.53	33.40
4.	Pond Disposal	7.65	9.30
		40.86	49.60

* Additions (to be prorated)

5.	Escalation	6.10
6.	Interest during Construction	2.64
		8.74

EXHIBIT II

PARTICULATE SCRUBBING ONLY (LOW-SULFUR COAL)
MULTI-UNIT RETROFIT OVER A
THREE-YEAR PERIOD

		PER KW	
		1971 COST	COST WITH PRORATED ADDITIONS*
1.	Lime Receiving, Storage, Slaking	.70	.90
2.	Scrubbing System, Solids Concentration	19.10	24.50
3.	Pond Disposal	4.02	5.10
*	Additions (to be prorated)		
4.	Escalation	4.87	
5.	Interest during Construction	1.81	
		6.68	

EXHIBIT III

OPERATING COSTS FOR WET LIMESTONE SCRUBBING PLANTS IN 200 - 300 Mw RANGE
- WITH POND* -

NON-VARIABLE COSTS:	Assumed Requirements	Per Ton of Coal
Capital charges	14 percent investment	
Maintenance	2 percent investment	
Laboratory	5-10,000 manhours	
Operating labor & supervision	15-30,000 manhours	
Sub-total	$2.1-6.6 MM/year =	$2.20-2.70 (depending on size)

VARIABLES COSTS:	Quantity per Ton of Coal	Assumed Unit Cost	Cost per Ton of Coal	Per Ton of Coal
Limestone	.20 T	$3 per Ton	.60	
Water	.35 Mgal.	$.15 per Mgal.	.05	
Power	100. Kwhr	$.006 per Kwhr	.60	
Steam (100^{o} reheat)	.90 Mlbs.	$.40 per Mlbs.	.35	
Sub-total				1.60
GRAND TOTAL, per Ton of Coal				$3.80-4.30 (depending on size)

---

* Wet waste disposal without pond	.55 T	$1 per Ton wet solids	$.55

EXHIBIT IV

OPERATING COSTS FOR WET PARTICULATE REMOVAL ONLY - WITH POND*

NON-VARIABLE COSTS:	Assumed Requirements:		Per Ton of Coal
Capital charges	14	percent investment	
Maintenance	2	percent investment	
Laboratory	3-7,000	manhours	
Operating labor & supervision	10-20,000	manhours	
Sub-total	$1.3-4.1 MM/year =		$1.35-1.70

VARIABLE COSTS:	Quantity per Ton of Coal	Assumed Unit Cost	Cost per Ton of Coal	
Lime	.02 T	$18	.36	
Water	.35 Mgal.	$.15	.05	
Power	60. Kwhr	$.006	.36	
Steam (100° reheat)	.90 Mlbs.	$.40	.35	
Sub-total				1.12
GRAND TOTAL, per Ton of Coal				$2.47-2.82

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* Wet waste disposal without pond .25 $1 $.25

EXHIBIT V

TYPICAL MAINTENANCE FOR COKE PLANT

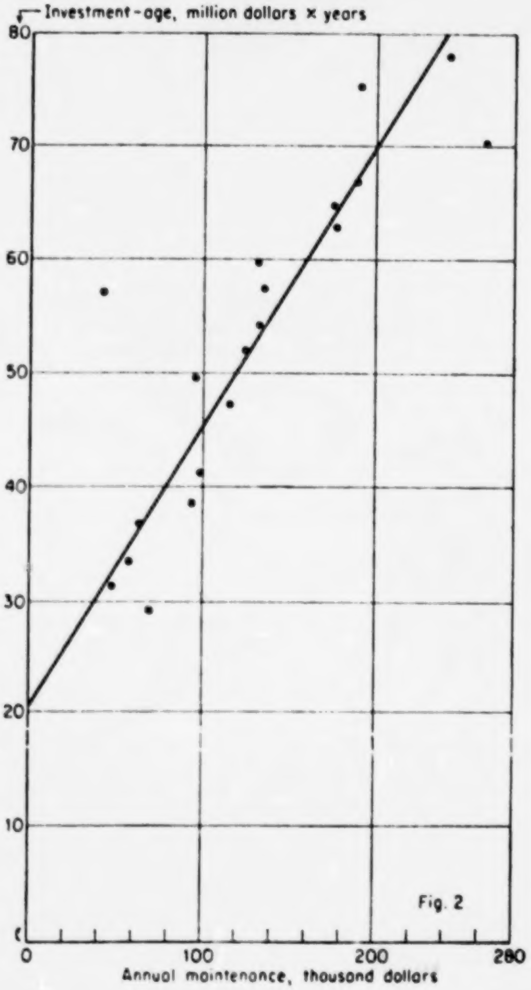


Fig. 2

$$M = 0.004\ I \times t - 83,100$$

where M = annual maintenance
I = investment
t = age, years

Source: Chem. Eng.

EXHIBIT VI

EFFECT OF CHEMICAL REACTION ON THE TRANSFER AND STORAGE OF FILTER CAKE

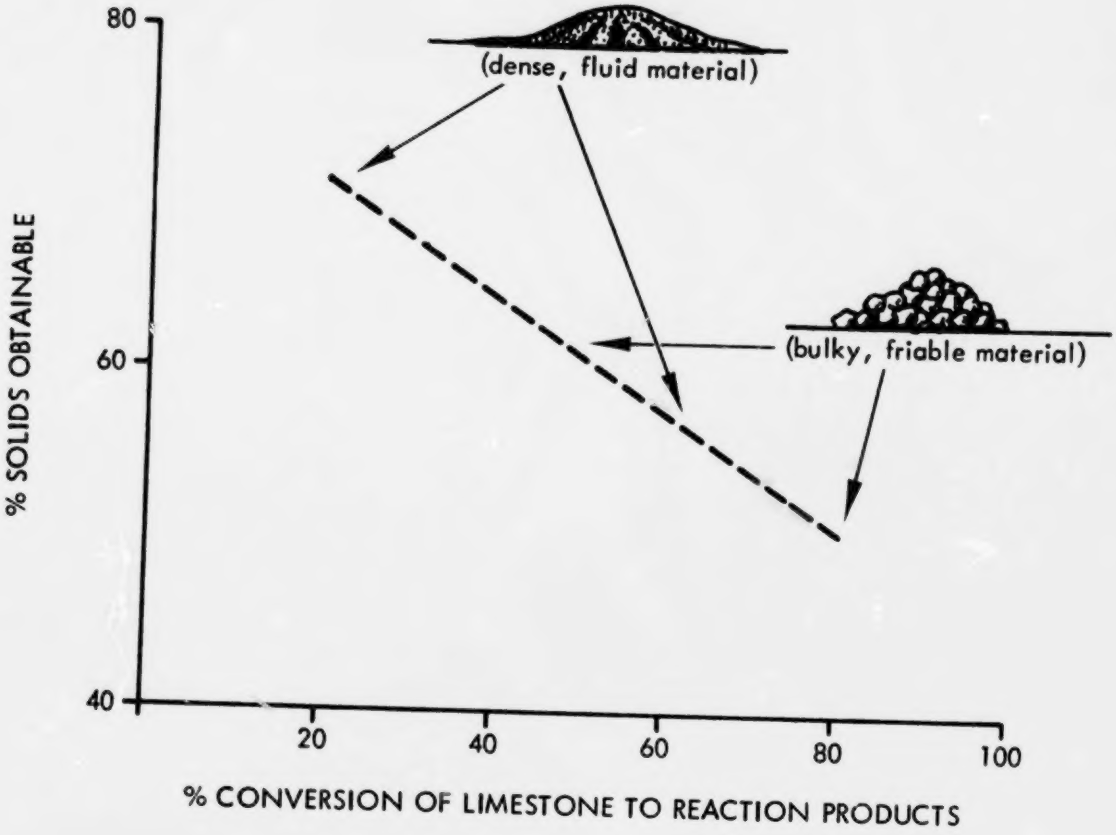
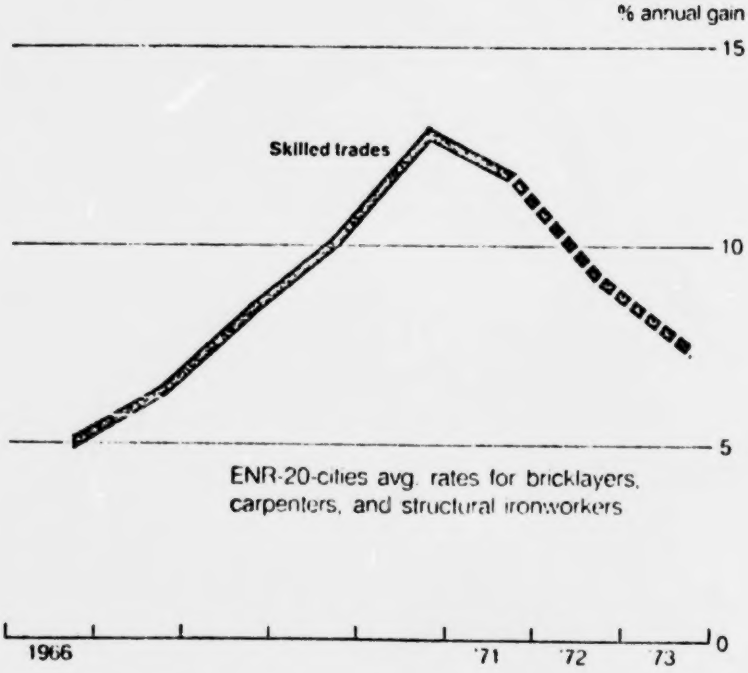


EXHIBIT VII

ESCALATION



ENR-20-cities avg. rates for bricklayers, carpenters, and structural ironworkers

Source: ENR

THE RC/BAHCO SYSTEM FOR REMOVAL OF SULFUR OXIDES AND FLY ASH FROM FLUE GASES

By

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Presentation at Second International Lime/Limestone-Wet Scrubbing Symposium

New Orleans, Louisiana

November 8-12, 1971

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INTRODUCTION

The first widespread application of a flue gas desulfurization system appears to be underway. There are a number of variations on the theme but basically it appears that a throw-away calcium based scrubbing system offers the most feasible alternative at this point in time. Research-Cottrell in the belief that no one system can meet the needs of the total market has endeavored to provide a number of systems. One of these systems which utilizes a packed tower has been previously described at this symposium.[1] A second and completely distinct system now being offered by Research-Cottrell under license from Bahco will be reported on in this paper.

In 1964, AB Bahco of Sweden initiated investigation of sulfur dioxide control and after preliminary screening studies, decided to develop a calcium based scrubbing system.

In 1966, AB Bahco installed a 1400 scfm pilot unit at their central heating plant. This facility was operated for three heating seasons, and studies were conducted on hydrated lime, burned lime and limestone. Results obtained during this operation were previously reported by Gustavsson.[2]

The first commercial installation of the system went into operation in November, 1969, at Södersjukhuset, a large hospital in Stockholm. With the success of the first unit, two additional units were installed at that site. Each unit accommodates an oil fired steam boiler with a capacity of 33 metric tons of steam per hour. The first slide shows the installation at Södersjukhuset.

Gustavsson's[3] paper presented at the 1st International Lime/Limestone Symposium indicated that this system was significantly beyond any other in its stage of commercial development. That symposium fostered the Research-Cottrell - Bahco relationship which culminated in their recent license agreement. In order for Research-Cottrell to arrive at a decision to proceed with the licensing negotiation, a rigorous techno-economic and market evaluation of the Bahco SO_2 removal system first had to be executed. Portions of the techno-economic evaluation will be reported on here.

PROCESS DESCRIPTION

Figure 1 illustrates the major functions of the RC/BAHCO two-stage scrubber. Flue gas is supplied by an I.D. fan with the typical draft control mechanism. A secondary damper, which admits make-up air and automatically maintains optimum gas flow in the scrubber during varying boiler operations, is connected to the vacuum side of the I.D. fan.

Flue gas is forced into the scrubber inlet (1) where it is distributed and directed against the surface of a hydrated lime slurry. There the flue gas reverses direction and enters the first venturi stage (2). The gas liquid contacting creates a vigorous cascade of droplets.

Due to the large flue gas velocity in the column inlet, the droplets are transported through the venturi scrubber at a high concentration and turbulence. The droplets are separated from the flue gas in a centrifugal force drop collector (3). Liquid is returned to the first stage contact zone and the gas passes to the second stage venturi (4) where the gas-liquid contact process is repeated.

In the second stage drop collector (5), the gas becomes free of droplets and exits through the chimney (6). The scrubbing liquid (13) is recirculated to the first stage contact zone (14). The scrubbing liquid is milk of lime prepared by dissolving slaked lime in water.

The slaked lime is fed from a bin (7) by a screw conveyor (8) through a mixer (9) into a dissolver (10). From the dissolver, the milk of lime is pumped to the second stage impingement zone (11) where the liquid height is controlled by a level tank (12). The liquid overflow is recirculated to the mixer.

The lower scrubber stage is provided with partially spent slurry from the two drop collectors. The overflow returns to the dissolver, which is also the level tank for the first stage. A regulator keeps the level constant in the dissolver by supplying fresh water.

A fraction of the return flow from the first drop collector (16) is continuously separated using a concentration regulator (17) into a thickener (18) which automatically feeds viscous waste sludge into a large basin (19). Sludge then can be pumped to a storage truck for transport to a refuse dump.

Alternately, the sludge can be pumped to a settling pond or disposed of directly; another option would be filtration of the clarifier bottoms to achieve a higher solids content before trucking.

PERFORMANCE

In December, 1970, a team of Research-Cottrell's technical personnel visited Södersjukhuset in order to observe and test the Bahco SO_2 removal system. At that time, only Unit #1 was installed and operating. The main objectives of this visit were verification of the Bahco SO_2 removal claims and also observation of the system's operational reliability and simplicity. Particulate removal testing was not given priority at that time since Research-Cottrell believed that based on its extensive venturi scrubber experience it could reliably predict the particulate removal efficiency.

On-site observations of the unit were made for a three week period. During this time, the unit operated in a trouble free and reliable manner requiring very little attention. The scrubber operation was attended to by the same operator who serviced the boiler. His main task with respect to the scrubber was that of measuring the pH of the outlet slurry to the sedimentation tank. This he did hourly and this task required 10 minutes at the most.

Lime delivery was observed twice. The lime was pneumatically delivered from the truck through a rubber hose to the lime hopper. This task required about thirty minutes and was wholly performed by the truck driver.

Waste removal was observed once. The sludge was pumped to the removal truck and this task was performed again solely by the truck driver.

An interview of the hospital's chief engineer indicated that the greatest problem encountered in the first season's operation of the Bahco scrubber was that the dampers and flow measuring devices became inoperable at the very low ambient temperatures prevalent (-25°C). The sludge handling portion of the unit, therefore, had to be insulated. At the end of the first season's operation (i.e. seven months), the unit was still operable even though there was about one inch of build up on the wall. The end of the season cleaning was executed manually by three men in thirty-two hours.

Assessment of Performance

While at Södersjukhuset, CES personnel measured overall SO_2 removal efficiencies of the Bahco system. These tests confirmed the efficiency claims of Bahco.

Due to the unseasonably mild weather enjoyed by Stockholm residents during the first three weeks of December, the boiler was only operating at 30% of full capacity. The average steam production was 10 metric tons per hour at a pressure of 24.0 Kg/cm^2 (341 psi) and temperature of 360° C. Heavy #4 oil with a sulfur content of approximately 1.5% was consumed at an average rate of 800 liters/hour. The scrubber was operated at an average pressure drop of 400 mm (15.7" water) and a pH of 5.5-6.0. Lime consumption was about 70 lbs/hour. Make-up air, introduced via a calibrated mechanical damper, was mixed with the flue gas before entering the scrubber to insure a constant liquid to gas ratio.

The gas stream was sampled simultaneously at the inlet (before make-up air is introduced) and the outlet of the scrubber. The gas was absorbed in 150 ml of 3% hydrogen peroxide for eleven minutes at a rate of 0.4 cfm. A suitable sample was extracted and titrated with 0.1 N sodium hydroxide to a methyl-orange endpoint. Three different tests verified the Bahco claims of high SO_2 removal efficiency. These tests are shown in Table 1. A comparison of these results with Bahco data are shown in Figure 2. It must be noted that the values obtained for SO_2 concentration at the inlet are actual measurements of SO_2 concentration coming from the boiler and need to be adjusted for the dilution of fresh air.

ECONOMICS

A plot of RC/Bahco system capital costs versus gas volume is shown in Figure 3. Represented here are the estimated bugetary selling price for an installed module; thus, all equipment shown in Figure 1 are included. This, however, is not a turnkey cost; and, as such, does not include any unique installation costs such as interconnecting duct work, utility connections, remote instrumentation, etc. Turnkey* costs are often significantly higher than installed costs for historical air pollution control applications.

Operating costs for a single case have been provided in Table 3. Here it is shown that for a 40 megawatt unit, the annual operating cost would be about $316,000. The largest single item is the lime cost at about 57% of the total. The second largest is the power at about 13% of the total. The corresponding material balance is shown in Table 2.

---

* Total installed system cost.

Figure 4 illustrates the annualized cost of operating a RC/Bahco SO_2 scrubbing system for various flue gas SO_2 concentration levels and unit sizes. The scrubbing annualized operating costs are also compared with an assumed cost of a fuel switching option for meeting pending SO_2 legislation requirements.

SUMMARY

In 1970, Bahco licensed their system for the Japanese market. A number of installations are already in operation in Japan. A list of the systems sold to date are provided in Table 4. The last group of slides show the installation at Yoshinaga. This installation consists of three units each with a gas handling capacity of 44,000 scfm. The units are installed on oil fired boilers and employ sodium hydroxide scrubbing. The reaction product is used in the pulping process.

At this time, Research-Cottrell intends to apply the system to fossil fuel boilers with capacities in the range of 60,000 to 500,000 pounds of steam. It is anticipated that once Research-Cottrell is fully geared up to respond to the market, the delivery time will be nine months. Discussions are presently underway with a number of companies for application of the system to both utility and industrial boilers.

REFERENCES

1. Gleason, R. J., "Limestone Scrubbing Efficiency of Sulfur Dioxide In A Wetted Film Packed Tower In Series With A Venturi Scrubber", Paper presented at the Second International Lime/Limestone-Wet Scrubbing Symposium, November 10, 1971, New Orleans, Louisiana.

2. Gustavsson, C. A., "Bahco SO_2-Scrubber CTB-CTK 1.5 Pilot Plant Connected to Bahco's Central Heating Plant", Paper presented at 1st International Lime/Limestone Symposium, March, 1970, Pensacola, Florida.

3. Gustavsson, C. A., "Bahco SO_2-Scrubber, Commercial Installation at Södersjukhuset, a Swedish Hospital in Stockholm", Paper presented at 1st International Lime/Limestone Symposium, March, 1970, Pensacola, Florida.

TABLE I

TESTS AT SODERSJUKHUSET SITE OF BAHCO SCRUBBERS

	BOILER				SCRUBBER				SO_2 ppm			
Test # & Date	Press. Kg/cm^2	Tons/hr. Metric	Temp. °C	Oil Cons. Liters	mm H_2O Δp	pH	Inlet Temp. °C	Outlet Temp. °C	In	Out	Fresh Air Dil. Nm^3/hr.	SO_2 % Eff.
2 12/9/70	24.0	10.0	340	920	410	5.8	110	38	620	7.5	27,000	96.2
3 12/9/70	24.0	10.0	340	920	400	6.2	100	38	690	5.5	27,500	97.5
4 12/10/70	24.0	10.2	340	790	410	6.0	100	39	645	5.2	31,600	96.6

TABLE 2

MATERIAL BALANCE

BAHCO PLANT SIZE--40 MW

	IN	OUT
GAS		
VOL (ACFM)	137,000	104,000
TEMP (° F)	350°	135°
SO_2 (PPM)	2,000	60
DUST LOAD (GR/SCFD)	2.4	0.024
SLUDGE		
(T/HR) (50% Solids)	-----------	5.88
RAW MATERIAL		
LIME (91% CaO)(T/HR)	0.94	-----------
WATER (GAL/MIN)	37	-----------

TABLE 3

Estimated Annual Operating Costs

For

40MW RC/Bahco SO_2 System

Utilities	Quantity Required	Cost $/Unit	Annual Cost (1) $/yr
Power	600 KW	0.008 $/KW hr	42,400
Make-up Water	40 gpm	0.3 $/1,000 gal	6,300
Chemicals			
Lime (91% CaO)	0.935 tons/hr	22.0 $/ton (2)	180,000
Other Operating Expenses			
Operators	0.5 man/shift	4.0 $/hr	17,500
Supervision (25% labor)			4,400
Maintenance (3% of capital cost)			20,200
Direct Overhead (75% of Labor & Maintenance)			31,600
Taxes and Insurance (2% of capital cost)			13,500
Estimated Operating Costs			$315,900

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(1) Assumes 8,760 hours/year; does not include waste disposal cost or gas reheat cost.

(2) Includes delivery; i.e., lime trucked approximately 50 miles.

TABLE 4
INSTALLATION OF THE BAHCO SO_2 REMOVAL SYSTEM

COMPANY	LOCATION	NUMBER OF UNITS	UNIT CAPACITY SCFM	SCRUBBING REAGENT
SÖDERSJUKHUSET	STOCKHOLM	3	17,700	$Ca(OH)_2$
DAISHOWA SEISHI COMPANY	SUZUKAWA	1	14,700	NaOH
DAISHOWA SEISHI COMPANY	YOSHINAGA	3	44,200	NaOH
OSAKA CITY	OSAKA	1	10,000	NaOH
HIROSHIMA CITY	HIROSHIMA	1	10,000	NaOH
YAHAGI IRON WORKS	NAGOYA	1	48,300	$Ca(OH)_2$
TAIO PAPER COMPANY	EHIME	1 1	83,000 66,400	NaOH NaOH
CENTRAL GLASS COMPANY	SAKAI	1	31,300	NaOH

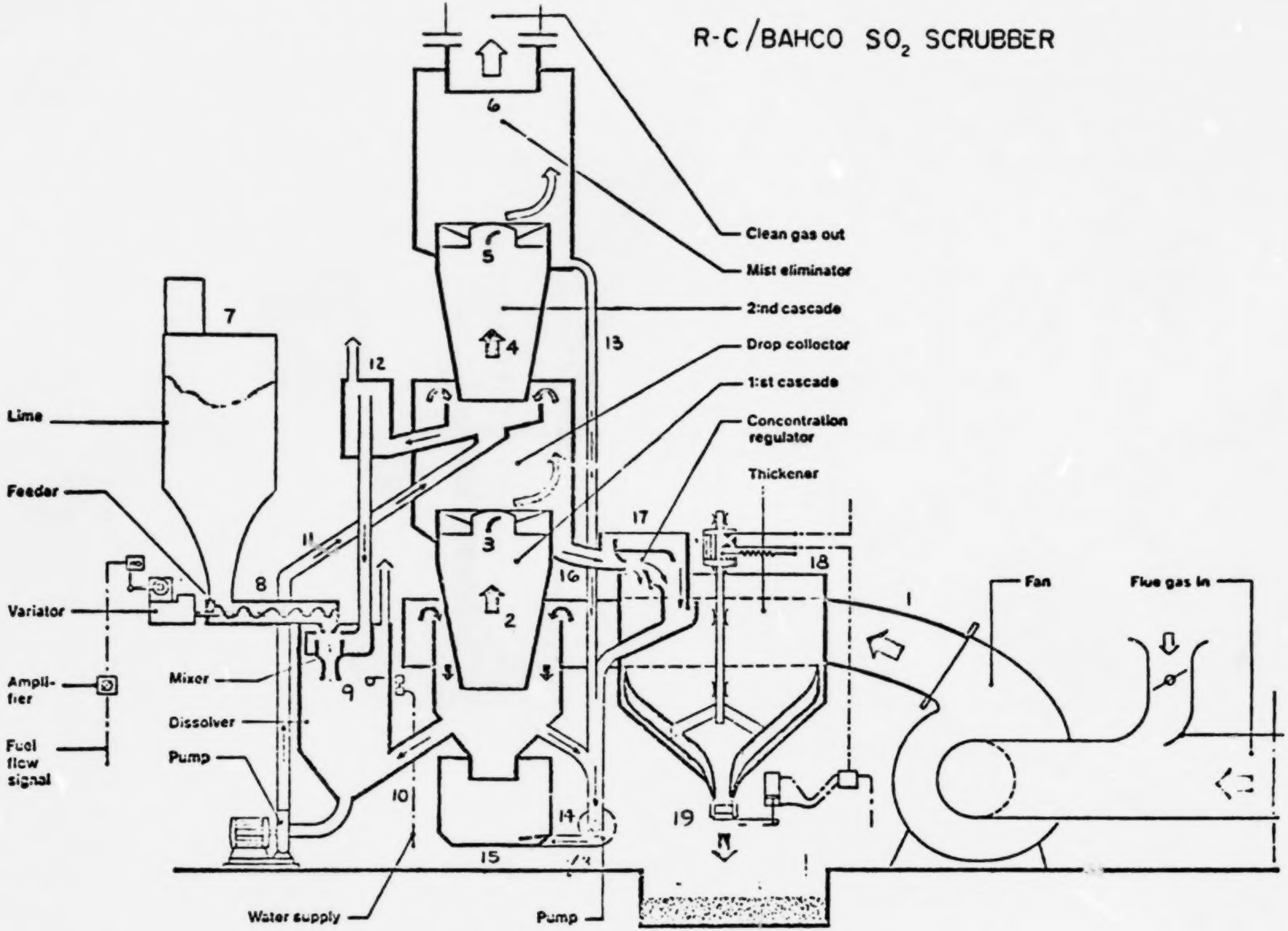

R-C/BAHCO SO$_2$ SCRUBBER
Clean gas out
Mist eliminator
2:nd cascade
Drop collector
1:st cascade
Concentration regulator
Thickener
Fan
Flue gas in
Lime
Feeder
Variator
Amplifier
Fuel flow signal
Mixer
Dissolver
Pump
Water supply
Pump
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

FIGURE 1

FIGURE 2

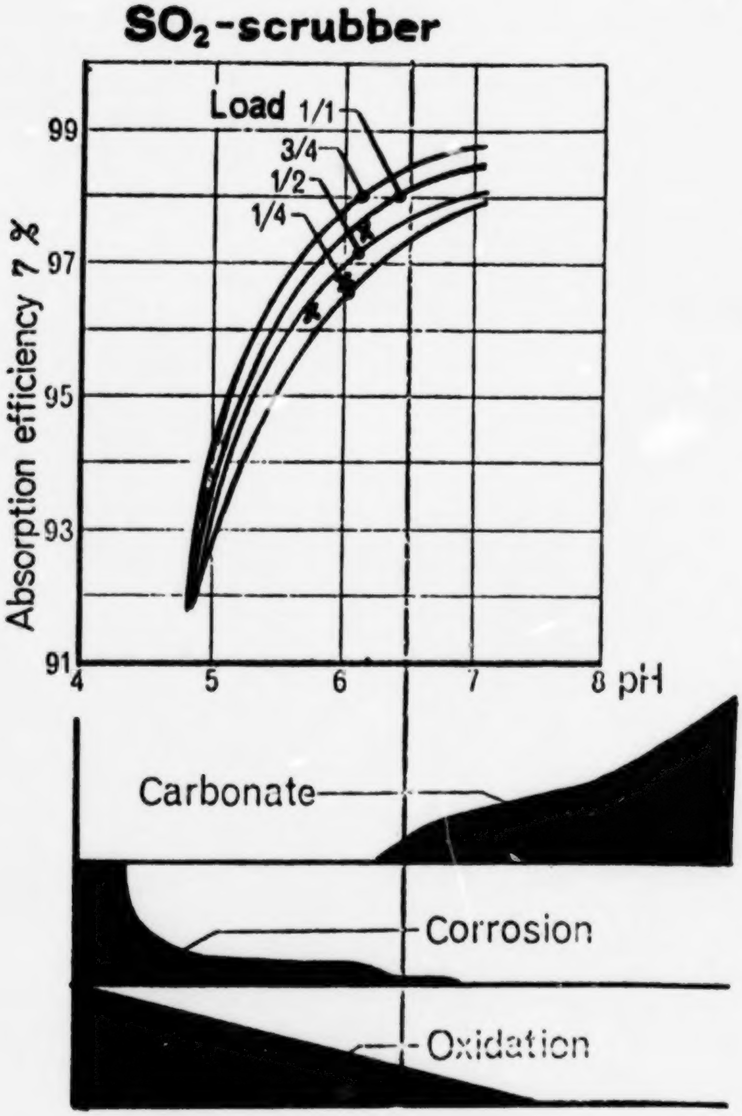
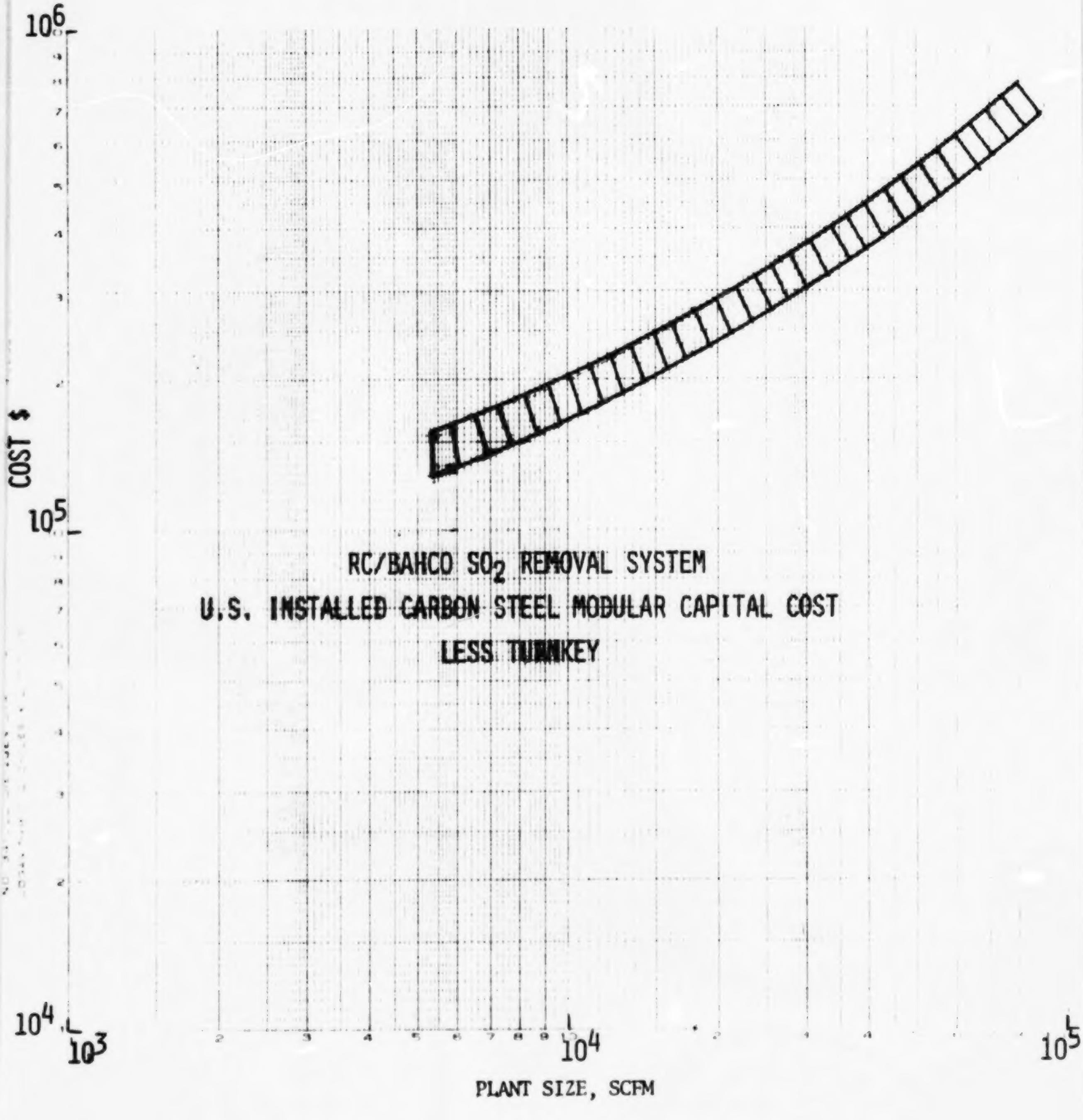

SO₂-scrubber
Load 1/1
3/4
1/2
1/4
99
97
95
93
91
Absorption efficiency η %
4
5
6
7
8 pH
Carbonate
Corrosion
Oxidation

FIGURE 3



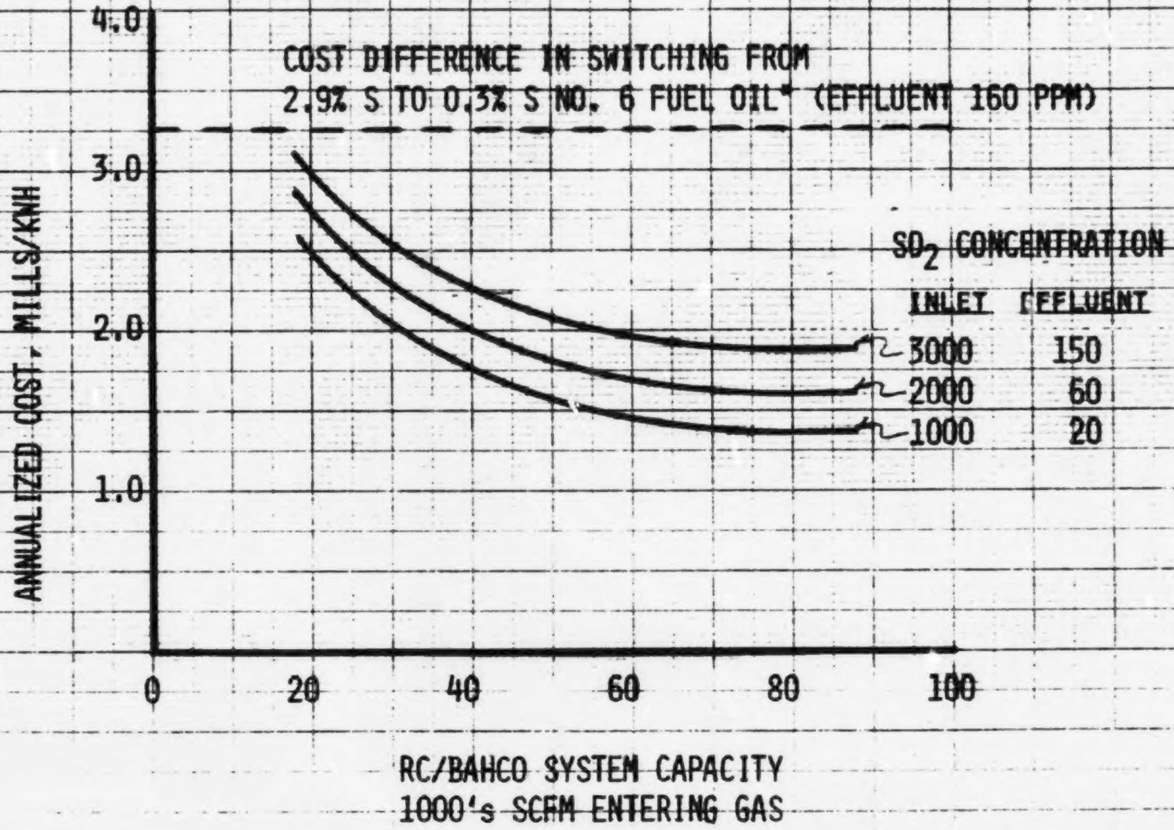
RC/BAHCO SO_2 REMOVAL SYSTEM

U.S. INSTALLED CARBON STEEL MODULAR CAPITAL COST

LESS TURNKEY

FIGURE 4

ANNUALIZED COST/FUEL SWITCHING COMPARISON



(ASSUMED INDUSTRIAL SITUATION WITH 50% UNIT UTILIZATION)

*WALL STREET JOURNAL 9/23/71

THE BISCHOFF PROCESS--INITIAL RESULTS FROM A FULL-SIZE EXPERIMENTAL PLANT

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Gottfried Bischoff
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Presented by:
Ulrich Kleeberg

Prepared for
Second International Lime/Limestone
Wet Scrubbing Symposium
New Orleans, Louisiana
November 8-12, 1971

The Bischoff Process - Initial results from a full-size experimental plant

by Dr.-Ing. Gerhard Hausberg

For reasons well known it is advisable to use experimental plants of the greatest possible size to gain knowledge on the reactions and transitional processes taking place in heterogeneous mass flows.

The flow rates through such experimental units should be approximately comparable to the partial streams passing through each of the several units that are connected in parallel in high-capacity commercial plants. Taking, for example, six scrubbers connected in parallel for an 800-MW boiler, than each group will have to handle a flue gas rate of approximately 500 000 m^3NTP/h.

Scrubbers of the same design for flow rates of this magnitude and even of up to 10^6 m^3/NTP/h have been in use for several years in the iron and steel industries.

The tests we carried out in 1968 and 1969 in a pilot plant designed for a maximum throughput rate of 5 000 m^3NTP/h were from the outset regarded as preliminary tests only. There was agreement that whatever results would be obtained from this pilot plant they certainly could not be used without further experience as basis for engineering full-size commercial plants.

An initial report on the resuls obtained with the pilot plant was given in October 1969.

Although the informative value and usefulness of the data derived from small scale plants are often higher than what one would expect in view of the equipolent influence of several laws of similarity, the only thing it was hoped could be gained from the pilot plant was an adequate justification for planning and building a much larger experimental unit. Since the results obtained from the small version were indeed encouraging, the decision was made, early in 1970, to go ahead with a full-size experimental plant for a flue gas throughput of 140 000 m^3NTP/h. This plant, which was installed in the Steag power station of Kellermann at Lünen, West Germany, went into operation at the beginning of February 1971.

The large scrubber unit is, basically, of the same design as that of the small version, which had been dismantled in the meantime and which is now being used in a steel plant. Owing to the fact that the full-size unit is located immediately after the new 350-MW boiler of the Kellermann power generating unit, minor changes in the dimensional proportions had to be made. The throughput ratio between the two units is approximately 30:1.

Fig. 1 gives a size comparison between the two experimental units.

The scrubber of the large unit is again a two-stage design with centrally disposed spiral jet nozzles, some of which are of the double-sided type. The raw gas pipe has initially been connected to the boiler at a point upstream of the electrostatic precipitator and enters the primary scrubber stage at the top. The flue gases flow at first only through the primary scrubbing and cooling zone which has no internals other than the spiral jet nozzles.

The second stage is accommodated in the same circular cylindrical housing. It contains an adjustable annular gap washer. The two stages are separated from one another by a sloping plate. The scrubbing fluid for the second stage is injected through a spiral jet nozzle also arranged in the centre of the housing.

Downstream of the annular gap washer, the gas flows through a water separator of the axial-flow rotor type whereby the residual water present in the form of droplets is removed by centrifugal effect.

The induced draft fan arranged at the downstream end of the system is provided with variable-pitch guide vanes. In combination with the adjustable annular gap washer it permits the system to be operated at a constant pressure differential while the flue gas rate varies. The clean gas leaving the scrubber passes through the clean gas flues to the power station stack. With the system operating at full capacity, approximately 10 per cent of the flue gas volume discharged from the 350-MW boiler passes through the scrubber.

With the present system layout, all of the water required for the annular gap stage is taken from the overflow of the settling tank. This amount is withdrawn from the collecting tray of the secondary washer and passed to the two bottom nozzles of the primary scrubber.

Of the remaining amount of water needed for the primary stage, only that quantity required for the annular gap stage is pumped to the settling tank. The larger portion is taken from the collecting tray of the first stage and directly injected again into the primary scrubber. In the tests still to be run, the layout of the water cycles will be varied in several ways, although at the present stage no details can be given. An elevated circular cylindrical vessel with central inlet and conical bottom section is used for clarifying and settling.

The next illustration (2) shows the general layout of the system with its water circuits.

The sludge accumulating in the conical discharge section of the settling tank is pumped to the dump area by a slurry pump via a plastic pipe over a distance of abt. 700 m.

Before the tests were started, three wells were drilled in the area where the sludge was to be dumped and the ground water was analyzed in its original condition. After the tests were begun and sludge dumped in this area, the ground water was checked at regular intervals.

Like in the small-scale plant, dry pulverized white lime is still being used as alkaline additive in the full-size unit. The material is introduced through a vertical pipe arranged centrally in the raw gas inlet. A proportional belt weigher located at the lime bin serves to adjust the amount of lime fed into the system.

After the full-size plant was put into operation, the lime-to-SO_2 ratio was at first adjusted as far as possible to the values which experience gained with the pilot plant had shown to result in an SO_2 removal efficiency of around 80 per cent. The flue gas rate was varied in the range from 90 000 to 133 00 m^3NTP/h and the loss of head accross the annular gap washer held between 200 and 250 mm WG. So far, the system could not be operated at the maximum flue gas flow of 140 000 m^3 NTP/h as this would have led to a loss of head exceeding the maximum allowed value of 250 mm WG. Full-load tests will be run, however, after making a minor modification on the annular gap washer.

If we enter the values obtained from the full size plant in the SO_2 removal diagram plotted for the pilot plant, then, as we see from the next slide (3), the values already known are largely confirmed by the full-size plant.

In this connection, it should be noted however, that the raw gas from the 350-MW boiler contained between 3,0 and 5,0 g/m^3NTP of SO_2, that is, about 1,5 g/m^3NTP or 0,0525 per cent by volume more than the flue gas of the small boiler with liquid ash discharge.

It is also apparent from Fig. 3 that the flue gas volume, and hence, the period of detention do not exercise any distinct influence within the range of the throughput rates used. This may be due to the fact that the effects of several process parameters partly cancel each other. For example, it is not possible to determine what influence the SO_2 content of the raw gas has on the removal efficiency, as the concentration of SO_2 in the raw gas from the 350-MW boiler was constantly fluctuating within the above-mentioned range.

Messurements made to check the dust removal efficiency of the full-scale plant showed that dust concentration in the clean gas was 50 mg/m^3NTP when the system throughput was 133 000 m^3NTP/h and the dust load of the raw gas was 15 g/m^3NTP. The removal efficiency, therefore, on average was 99,7 per cent.

In the small-scale unit, dust concentration in the clean gas ranged between 10 and 15 mg/m^3NTP at a mean entry concentration of abt. 10 g/m^3NTP. The light coloured, yelloish grey fly ash of the 350-MW boiler appears to be much finer than the much darker ash from the small boiler with liquid ash discharge. So far, no dust analyses have been made.

The final dust concentration of 50 mg/m^3NTP obtained with the full-size plant is far below the maximum allowable value of 150 mg/m^3NTP.

With the knowledge now available on SO_2 and dust removal and its dependence on volume flow, it would be possible to build units for throughput rates of, say, $10^6 m^3$NTP/h and over, based on the tested design and layout.

While the tests so far have proved in the main that the results obtained with the pilot plant with respect to separation efficiency also apply to the full-size version, the purpose of further tests will be to try out a series of designs and process variants some of which are aimed at an optimization of the dimensions of the primary scrubbing stage. Operational reliability will be the most important aspect.

Reproducibility of guaranteed values in continuous operation at a minimum of maintenance costs is the standard by which operational reliability must be gauged. Therefore, one thing for which the full-size plant was constantly being observed and checked was the formation of deposits and incrustations.

It was particularly in the conical section and in the upper third of the cylindrical shell of the scrubber that substantial incrustations and asymmetrical deposits, due to the given inflow conditions, occurred.

After the design was changed to give better flow conditions and additional spray nozzles for intensive shell washing, as shown in Fig. (4), were installed, a considerable improvement was obtained.

By varying the rate of wash water flow at constant gas throughput, it was proved that the rate of growth of the deposits on the shell surface was essentially dependent on the thickness and velocity of the film running down the shell surface.

A temporary disturbance in the operation of the full-size unit occurred as a result of insufficient clarification of the return water. In designing the settling tank, the dimensions had intentionally been held rather small because plans were for this part of the system to be extended only at a later stage. It thus could happen that the water recycled to the scrubber was for a while entering the annular gap washer as a slurry containing 200 g/l of solids. While this appeared to have no influence on SO_2 and dust removal, and the nozzles were not clogged, heavy erosion must be expected to occur in the long run on such items as pumps, flow restrictors and nozzles.

After the inflow conditions and the pump-out conditions at the discharge cone of the elevated vessel were improved, the solids concentration in the overflow dropped to between 10 and 20 g/l. It is intended to test still other settling tanks of modified design and with larger dimensions. In this connection, it is noted that the mean settling velocity at concentrations up to 50 g/l was about 4 m/h and that it slowed to 1 m/h at a solids concentration of 100 g/l.

The slurry forming in the conical thickening section of the settling tank contains an average concentration of solids of abt. 300 g/l. Tests carried out by Westfalia Separator of Oelde, West Germany, have shown that this sludge water can be largely clarified with the aid of decanters. Residual water in the solids discharge is as low as abt. 30 per cent by weight. In spite of this low water content, the mixture still flows and can be pumped, and it may greatly reduce handling and dumping costs.

But since it was not our intention to content ourselves with dumping the sludge, we requested three institutions and specialist firms to cooperate in analyzing the sludge and studying the possibilities of processing it for commercial use.

Initial results of these studies indicate that it will be possible, for example, to use the sludge consisting of fly ash and reaction products as an additive in the production of lime sand bricks. Test bodies made by Rheinisch-Westfälische Kalkwerke, Dornap, using a 20-per cent addition of sludge were found to have a maximum compressive strength of 300 kgf/cm^2 as compared with 240 kgf/cm^2 for the standard lime sand brick.

In this connection it should be noted that gypsum in the form of dihydrate was found at the time in the sludge of the pilot plant in addition to the hemihydrate. In contrast to this , calcium sulphate in the form of anhydrite was in some instances found to prevail in the full-size plant.

One reason for this may be temperature zone differences between the two systems.

For instance, one point where dihydrate is converted into anhydrite is around 40 deg C. Moreover, as is known, the conversion points may shift owing to the presence of attendant materials, such as certain constituents of the fly ash. Part of the heat generated during the slaking of CaO will surely be dissipated more quickly in the small unit than in the larger plant.

Another use of the sludge seems possible if the gypsum produced in the process is again obtained in the form of dihydrate. If a unit for dry separation of fly ash is arranged to precede the scrubber, then it will be possible to produce high-quality gypsum board by the well known Giulini process.

After completion of the first set of test runs, the full-size plant will, therefore, be connected to follow the electrostatic precipitator so that measurements can be made for separate removal of dust and SO_2.

The fact should be emphasized here that it is not possible at the present stage to make a final statement on the sludge produced, because only a few samples were tested so far.

After completion of the tests in which pulverized white lime is injected into the raw gas inlet, the plant will be operated on milk of lime. It can be expected that the use of this additive in the form of slaked lime or calcium hydroxide will result in a further improvement of SO_2 removal. This was seen to be the case with the small pilot plant in which pulverized calcium hydroxide and milk of lime were used at times. In those tests a removal efficiency of 88,8 per cent was obtained at a concentration in the raw gas of only 2,25 g/m^3 NTP or approximately 0,08 per cent by volume.

The use of milk of lime will offer still another advantage. So far, all of the additive was introduced, as already mentioned, upstream of the primary scrubbing stage. The annular gap washer, operating in a zone of lesser concentration, received no additional lime. A check on the pH values of the wash fluid passing through the annular gap indicated 11,0 for the inflow and 5,5 for the outflow of that stage.

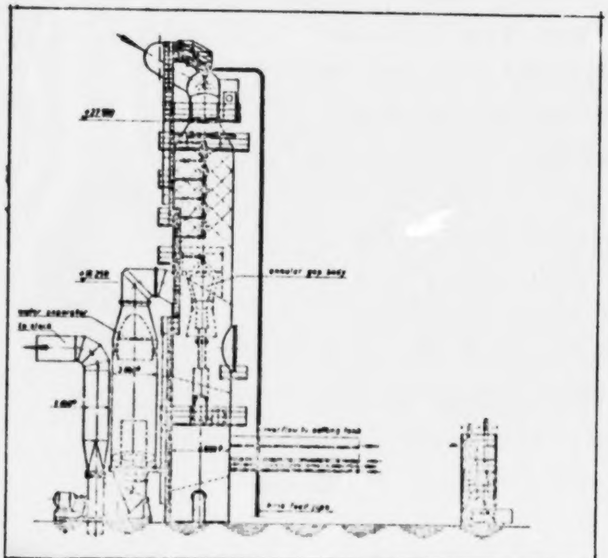
This means that the annular gap washer was working partly in the acid range.

When we change to milk of lime, we shall feed the additive to both stages in varying proportions.

The first and most important result of the tests run so far with the full-size plant is the fact that the information obtained with respect to SO_2 and dust removal is also applicable to the design and layout of large commercial units.

The tests were again prepared and carried out in close cooperation with Steinkohlen-Elektrizitätsgesellschaft-AG, Essen, which has proved so successful in the past.

L. Hausberg



Removal of SO_2 and dust from flue gases
Experimental units for 1[illegible]00 m³ NTP/h and 5,000 m³ NTP/h

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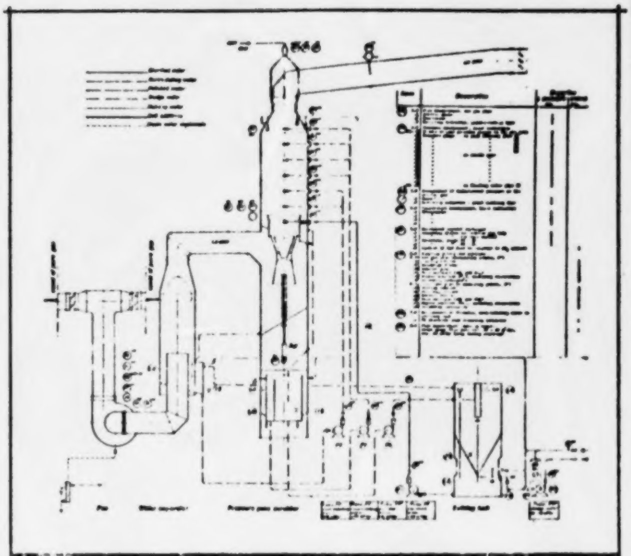
Ill. 1



Schematic Diagram of Plant for the Removal of Dust and SO_2 from Flue Gases

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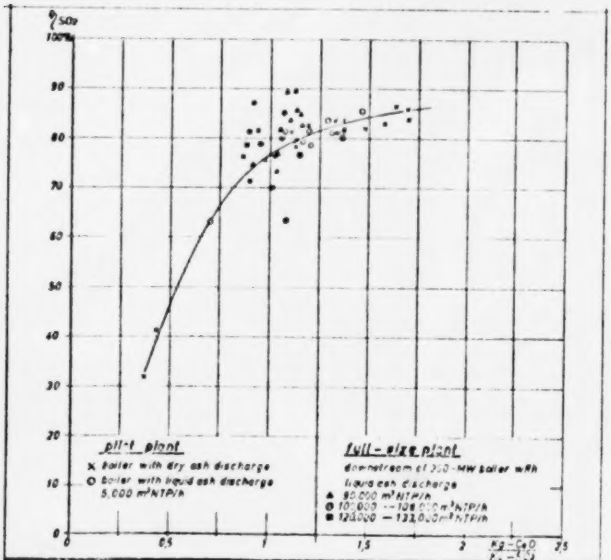
Ill. 2



SO_2-removal from flue gases

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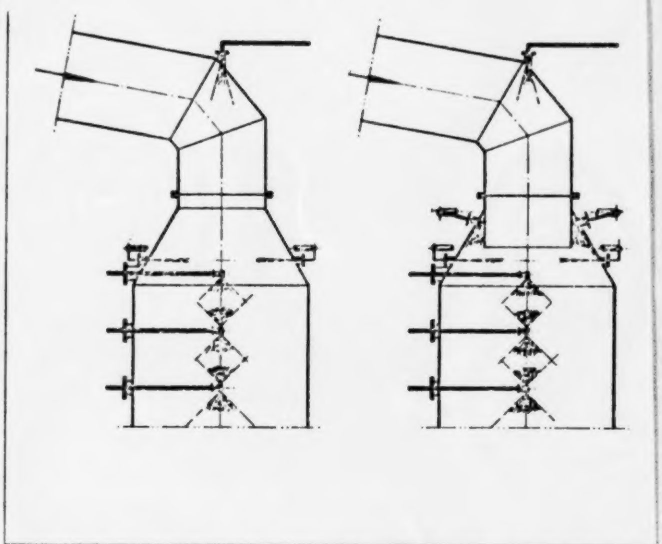
Ill. 3



SO_2 and dust removal from flue gases
full-size experimental plant – raw gas inlet

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Ill. 4

AVAILABILITY OF LIMESTONES AND DOLOMITES

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INTRODUCTION

Power in the United States is produced largely from plants which burn coal or oil as the primary fuel. The use of limestone or dolomite to control sulfur emissions from these plants is contingent upon several factors. Among these, proximity of adequate carbonate rock deposits to fossil fuel-fired power plants, and the relationship of carbonate rock production to possible demand are important considerations in establishing the relative merits of any carbonate rock-based process. This study, performed under contract with the Office of Air Programs, had as its objective the determination of the availability and costs of limestone and similar materials throughout the contiguous United States, thus providing a basis for determining the feasibility and economics of limestone-based SO_x removal processes for any particular power plant site.

POTENTIAL LIMESTONE DEMAND BY POWER PLANTS

Figure 1 shows the location of the major (≥200 MW) power plants in the United States which burn either coal or oil as the primary fuel. Included are a few plants which, although not yet constructed, are being designed exclusively for either coal or oil and are scheduled to be on stream by 1975. Of the 275 plants shown, 84% are coal-fired. The oil-fired plants are all located along the eastern coast, with most of these in the northeast. About 90% of all power plants shown are located east of the Mississippi River, with locally high concentrations in the northeastern quarter of the country, particularly in many of the major metropolitan areas.

Based on 1969 fuel consumption statistics, an estimated 20 million tons of sulfur oxides were emitted by power plants in the United States. More than 40 million tons of limestone would have been required to remove these oxides from the stack gases. This potential limestone demand has been broken down by region, with the regions being defined as follows:

Region	States Included
New England	Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, Vermont
Middle Atlantic	New Jersey, New York, Pennsylvania
East North Central	Illinois, Indiana, Michigan, Ohio, Wisconsin
West North Central	Iowa, Kansas, Minnesota, Missouri, Nebraska, North Dakota, South Dakota
South Atlantic	Delaware, Florida, Georgia, Maryland (incl. Washington, D.C.), North Carolina, South Carolina, Virginia, West Virginia
East South Central	Alabama, Kentucky, Mississippi, Tennessee
West South Central	Arkansas, Louisiana, Oklahoma, Texas
Mountain	Arizona, Colorado, Idaho, Montana, Nevada, New Mexico, Utah, Wyoming
Pacific	California, Oregon, Washington

Table 1 itemizes potential demand by region. The East North Central region far outranks any other region in potential limestone requirements with over one-third of the total. With the exception of New England, all regions in the eastern half of the country had potentially large demands for limestone.

CARBONATE ROCK RESOURCES

Deposits of carbonate rocks, including limestone, dolomite, shell, marble, and marl, occur in some form in every state. Total reserves have never been estimated, but are known to be enormous.

Figure 2 shows the distribution of surface carbonate rocks in the United States and includes limestone, dolomite, and marble. The map shows that surface deposits of carbonate rocks occur throughout the nation, but are particularly in evidence in the eastern half of the country. A band of deposits beginning in Vermont extends southward along the Appalachian Mountains into central Alabama. Extensive deposits are found in the states surrounding the Great Lakes, reaching southward into northern Alabama. Large areas of Minnesota, Iowa, and Missouri are covered with carbonate rocks and broad outcrops occur in Kansas, Oklahoma, Arkansas, and Texas.

Particularly in the central lowlands, carbonate rock deposits frequently occur as thick, horizontal formations covering large areas. In general, the deposits found in western states are different. They commonly occur as steeply dipping or vertical beds of small areal extent. However, notable exceptions to this are found, particularly in Colorado, Arizona, and New Mexico where large outcrops occur.

Limestone occurrences, including chalk but excluding dolomite, are shown in Figure 3. The map is similar to Figure 2 and shows that although limestone is found throughout the country, the more numerous and extensive deposits occur in the eastern half of the nation. In the western states, the deposits tend to be discontinuous and relatively small in areal extent.

The formations shown in Figure 3 include limestones of different degrees of purity. Estimates have been made that only about 2% of the known reserves of commercially usable limestone is chemical grade (> 95% carbonate content), and that the bulk of these reserves will be exhausted in 40-50 years. Much of this high purity limestone occurs in the area extending from the Great Lakes southward to Alabama.

Chalk deposits are shown in several of the central states and in a curving belt through Alabama and Mississippi. In general they are not high purity limestones, but locally they may contain over 95% calcium carbonate.

Figure 4 shows the location of high grade (>25% magnesium carbonate) dolomite quarries. Although originally drawn in 1941, it is a useful guide to the important occurrences of dolomite. As with limestone, the largest deposits are located in the eastern half of the country. Two major areas are noted. First, a belt of dolomite extends from Vermont to central Alabama, along the Appalachian Mountains. This coincides quite well with a similar band of limestone previously noted. Second, large formations of dolomite occur in the states encircling the Great Lakes. These deposits coincide with or adjoin large limestone deposits in the region.

The most significant deposits of marble are found along virtually the entire length of the Appalachian Mountains in the east, and as scattered occurrences in the Rocky Mountains in the west. Although eastern marbles are predominantly calcitic (high calcium), dolomitic types also occur. Both types are found in the west.

Shell limestone occurs primarily in Gulf Coastal waters, but it also is found in bay waters along both the east and west coasts. It is usually a very pure type of calcium carbonate.

Marl deposits exist in several areas, notably around the Great Lakes, and along the southeastern coastal plain. This soft, relatively impure form of calcium carbonate varies considerably in character, that of the Great Lakes area being a precipitated calcium carbonate, while that of the coastal plain is an impure shell deposit. Limited occurrences in other regions are generally impure chalks or soft limestones.

PRODUCTION

Crushed carbonate rock production in the United States in 1969 was distributed, by type, as indicated in Table 2. As shown, the total national production amounted to 652 million tons, of which over 85% was limestone. Dolomite ranked second with more than 10%. Marl and marble production were very low, amounting to less than 5 million tons combined, or 0.7% of the total.

No limestone production was reported in four states, viz., Louisiana, Delaware, New Hampshire, and North Dakota. In fact, the latter three states did not produce any type of carbonate rock. Dolomite was produced in twenty-four states, chiefly in the northeastern quarter of the country.

Production of limestone and dolomite, by region, is shown in Table 3. Within most regions, production rates of individual states varied from near zero to tens of millions of tons. The New England and Mountain regions, however, had fairly uniform (but low) outputs. The East North Central region was also exceptional, in that all states reported large quantities of limestone and dolomite, ranging from 16 million to 55 million tons. Nationwide, Pennsylvania and Illinois were the leading producers of limestone and dolomite, respectively.

Shell was dredged from bay waters along all three coasts. However, 83% came from Texas and Louisiana, with the latter being the leading producer. Small quantities of marl were produced in Indiana, Michigan, Minnesota, Mississippi, Nevada, South Carolina, Texas, and Virginia. Eighteen states, principally in eastern and western mountainous regions quarried marble, with Alabama recording the highest production at 632,000 tons.

Over 4,700 quarries, producing 861 million tons of crushed stone of all types, were in operation in the United States in 1969. Since production of crushed carbonate rocks totalled 652 million tons, it can be assumed that, roughly, over 3,500 of these quarries produced limestone, dolomite, and related stones. More than one-third of all quarries had annual production rates of less than 25,000 tons. The large operations (over 900,000 tons/year) produced one-third of the total crushed stone, although they represented less than 4% of the total number of quarries.

END USE

Carbonate rocks are unique among the different types used in this country. Not only do they find use in applications where their physical properties are important, but also in markets which utilize them for their chemical properties and composition. Almost two-thirds of the total production of carbonate rocks were used for various construction purposes in 1969. Most of this stone was used as an aggregate material in road construction. The second largest use was in cement manufacture, which consumed more than 105 million tons. About 70 million tons of high grade limestone and dolomite were used in lime manufacture and other applications requiring a high purity material.

SELLING PRICE

The average unit value, or net selling price at the quarry, for all crushed carbonate stones produced in the United States in 1969 was $1.49/ton and varied by type of stone as shown in Table 4. The average values ranged from a low of $1.01/ton for marl to a high of $9.69/ton for marble. The high unit value of marble reflects its primary use as a decorative material.

Unit value also varies with end use. Stone used for construction purposes averaged $1.44/ton while stone used in applications requiring a high purity material had an average value of $1.69/ton. Average prices ranged from $0.69/ton for fill to $6.00/ton for exposed aggregate (decorative stone). Stone for most applications, however, averaged under $2.00/ton. The variation in price depends not only on supply and demand, but also on the chemical and/or physical properties required for the particular application.

Average unit values of limestone and dolomite, by state, are shown in Table 5. Within most states, average prices were $1.00-2.00/ton, although spot prices ranged from $0.12-25.00/ton. New Jersey and several states in both the New England and Mountain regions reported average values greater than $2.00/ton. Rhode Island showed the highest average value: $7.57/ton for limestone. Prices shown for the Pacific region are unusual in that those for limestone are comparatively low while dolomite prices are quite high. In all cases where average unit values were high, production of the particular stone was limited.

With the exception of Virginia, which reported $3.92/ton, average prices of shell were $1.00-2.00/ton. Unit values for marl were all below $1.15/ton. Marble varied widely in price.

TRANSPORTATION

Trucks dominated in the transportation of carbonate rocks from quarry to consumer, accounting for almost three-fourths of all stone. Rail and waterway hauls, amounting to one-fifth of the stone shipments, were about equally divided.

Trucks generally are used for shorter hauls of under 50-100 miles, while rail is employed for longer distances. Where conditions permit, shipment of stone by barge or boat is preferred, since this is usually the cheapest method of transportation.

So many factors influence transportation rates and costs that it becomes very difficult to establish average rates, even within a single area. Most freight rates for crushed stone in the United States, however, fall within the ranges shown in Figures 5-7. The lower curves correspond to rates which could be obtained under favorable conditions; i.e., high volume movement, periodic shipments in lot-sized quantities, intrastate shipment or commodity rates, etc. The upper curves correspond to unfavorable conditions.

DELIVERED PRICE OF LIMESTONE

The delivered price of limestone to a power plant is the sum of the price of the stone at the quarry plus the transportation charges. To see what this actually would be, the delivered price of limestone to 37 selected power plants was determined based on the assumption that a high calcium limestone would be required. The results of this investigation are shown in Table 6.

Most of the plants are located in the eastern half of the United States where the major coal- and oil-fired power capacity is found. Prices range from $1.95-13.20/ton. Half of the plants could be supplied at under $4.00/ton, while all but 3 could obtain limestone at under $6.00/ton. The latter 3 plants are located in the west in areas where base prices are higher or limestone deposits are remote. For several eastern seaboard plants, particularly in New England, the availability of low-cost high calcium limestone is contingent upon the acceptability of an imported stone. Domestic sources are either inadequate or too distant to provide a low-cost material.

PROJECTED COSTS

Carbonate rocks historically have been stable, low-priced commodities. Based on average unit values for the years 1960-1969, projected average base prices for 1975 are as follows:

	1969	1975
Limestone and Dolomite	$1.45/ton	$1.67-1.82/ton
Marl	$1.01/ton	$1.28-1.48/ton

The average value of shell has dropped considerably since 1960. It is unlikely that it will continue to decrease through 1975. More probably, it will parallel limestone and dolomite but not exceed them in value. Average unit values for crushed marble are highly variable, reflecting the sensitivity of price to market conditions.

Transportation rates during the next few years should rise about 6%/year, on the average. Estimates by type of transportation are as follows:

Truck	4- 6%/year
Rail	6- 8%/year
Water	5-10%/year

In general, rate increases should follow wage increases granted to labor. The estimates, offered by stone producers, are predicated on the present state of the economy and a continuance of the present inflation rate. Any changes will, of course, affect these estimates.

SUPPLY/DEMAND RELATIONSHIP OF CARBONATE ROCKS FOR POLLUTION CONTROL

Proximity of Carbonate Rock Deposits to Power Plants

Comparison of Figures 1-4 indicates that the major deposits of carbonate rocks largely coincide in location with the power plants. This is particularly true in the East North Central region where huge reserves of stone occur. Both high calcium limestone and high grade dolomite abound, and many deposits are found near the major power generation centers throughout the region.

The New England region is not as fortunate. While the power plants are located primarily in coastal areas, the rock deposits occur in the mountainous western sections. Most of the deposits are highly crystalline stone or marble, and many are dolomitic. The suitability of these materials would have to be determined before including them as a possible source.

Availability of stone should not be a problem for power plants in the Middle Atlantic region. All types of stone occur and nearby deposits can be found. Plants in western and eastern Pennsylvania, particularly, are fortunate in that large reserves of high grade stones are present.

In the South Atlantic region, most plants are located near an adequate source of stone, particularly if the crystalline limestones and dolomites of the mountainous areas prove suitable. Several coastal plants could use shell or coral limestone, or marl. However, for some inland power plants in, for example, North Carolina, no nearby deposits exist.

Large quantites of high calcium limestone occur throughout the East South Central region and power plants should experience no difficulty in obtaining adequate supplies. Many plants located in Alabama and Tennessee also could obtain dolomite quite easily.

The less abundant and more widely scattered carbonate resources of the western states are of minor importance, since there are few coal-fired power plants in this area. With the exception of the two power plants located in North Dakota, which are far removed from any commercially important carbonate deposits, the few plants that do exist are fairly near reserves of high calcium stone.

Potential Demand Relative to Production

As previously mentioned, the potential demand for limestone by coal- and oil-fired power plants in 1969 exceeded 40 million tons. This represents only 7.3% of the national limestone production of 559 million tons. Dolomite production, on the other hand, was roughly 50% greater than the potential demand. Shell production was only one-half of the demand. The quantities of calcareous marl and crushed marble quarried were relatively insignificant. Obviously, limestone is the only stone produced in sufficient quantities to warrant nationwide consideration as an agent for SO_x removal. Dolomite and shell, however, are quarried in large enough amounts to make them important materials in some regions. Marl and crushed marble may be useful in certain localities where the other rocks do not exist, but their limited occurrence and production do not permit wide-scale use of these materials.

Table 7 shows the relationship of limestone and dolomite production to potential demand, by region and state. The third column of the table is the ratio of total limestone and dolomite production to potential demand, for 1969.

With the exception of New England, the eastern regions of the country all have large relative supplies of limestone and dolomite. There are, though, some exceptions to this among the individual states. New Jersey and Delaware have a potential need which exceeds their production. Adjacent states, however, are large producers of stone and could provide the necessary tonnages. Mississippi and both of the Carolinas have low relative supplies of stone. If they could not otherwise be supplied, marl deposits, which occur extensively in all three states, could be used. Georgia and West Virginia, with comparatively low relative supplies, could easily obtain needed stone from surrounding states. It is interesting to note that the region with the highest limestone demand, i.e., the East North Central region, also has the highest limestone and dolomite production.

The New England region faces a shortage of limestone and dolomite, with two states producing less stone than potentially required. The marble resources of the region could improve the situation somewhat, but power plants would have to rely on shipments of stone from nearby states such as New York, or, perhaps, on imports.

Most states in other regions of the country have ample production. North Dakota, with no production, is an outstanding exception to this, however. A few other states have low relative supplies of stone, but either the demand is quite small, or the production could easily be expanded to meet the need.

CONCLUSIONS

- Enormous deposits of carbonate rocks occur in the United States, and reserves are more than adequate for the foreseeable future. Availability of high purity stone may become a problem several decades hence, but, with the probability that the required quality will depend on other process and economic factors, no shortage of suitable stone is foreseen.

- The major deposits of carbonate rocks occur in the eastern half of the United States, where the vast majority of fossil fuel-fired power plants are located. Large reserves in these eastern areas provide a nearby source of stone for most power plants.

- Relative to the potential demand for carbonate rocks by power plants, production of these materials is quite large in most states. However, current production is inadequate to supply the potential needs of power plants in several Atlantic coastal regions, notably New England.

- Limestone is the only type of carbonate rock which is produced in large enough quantities to merit consideration for widespread application in the removal of SO_x from stack gases. In many areas, however, ample amounts of other carbonate rocks are produced, particularly dolomite.

- Most of the power plants in the eastern half of the United States could be supplied with high calcium limestone at less than $6.00/ton. Many could obtain stone at less than $4.00/ton. Costs for power plants located in western states generally would be higher, owing to the lack of suitable, nearby deposits.

- Based on projections of material cost and transportation charges to 1975, the delivered price of limestone to most power plants should not increase by more than $1.00-2.00/ton.

TABLE 1

POTENTIAL LIMESTONE DEMAND BY POWER PLANTS IN THE UNITED STATES

Region	Limestone (M Tons)	% of Total
New England	1,369	3.4
Middle Atlantic	6,583	16.2
East North Central	14,307	35.1
West North Central	2,738	6.7
South Atlantic	8,471	20.8
East South Central	5,645	13.9
West South Central	5	-
Mountain	1,351	3.3
Pacific	266	0.6
Total	40,735	100.0

TABLE 3

PRODUCTION OF CRUSHED AND BROKEN LIMESTONE AND DOLOMITE IN THE UNITED STATES IN 1969, BY REGION

Region	Production (MM Tons)
New England	2.4
Middle Atlantic	90.9
East North Central	185.6
West North Central	92.5
South Atlantic	87.5
East South Central	81.3
West South Central	58.3
Mountain	10.7
Pacific	18.8
Total	628.0

TABLE 2

PRODUCTION OF CRUSHED AND BROKEN CARBONATE STONES IN THE UNITED STATES IN 1969, BY TYPE

Type	Production (M Tons)
Limestone	558,793
Dolomite	68,380
Shell	19,731
Calcareous Marl	2,490
Marble	2,271
Total, All Types	651,665

TABLE 4

UNIT VALUE OF CRUSHED AND BROKEN CARBONATE STONES IN THE UNITED STATES IN 1969, BY TYPE

Type	Unit Value ($/Ton)
Limestone	1.45
Dolomite	1.55
Shell	1.42
Calcareous Marl	1.01
Marble	9.69
Average, All Types	1.49

TABLE 5

UNIT VALUE OF CRUSHED AND BROKEN LIMESTONE AND DOLOMITE IN THE UNITED STATES IN 1969, BY REGION AND STATE

Region and State	Average Unit Value ($/Ton)	
	Limestone	Dolomite
New England		
Connecticut	NR(1)	4.20
Maine	1.32	- (2)
Massachusetts	4.14	5.24
New Hampshire	-	-
Rhode Island	7.57	-
Vermont	1.46	1.53
Middle Atlantic		
New Jersey	2.49	-
New York	1.56	1.97
Pennsylvania	1.46	1.73
East North Central		
Illinois	1.44	1.45
Indiana	1.32	1.28
Michigan	1.02	1.45
Ohio	1.54	1.48
Wisconsin	1.17	1.21
West North Central		
Iowa	1.49	1.72
Kansas	1.40	-
Minnesota	1.32	1.38
Missouri	1.39	1.13
Nebraska	1.87	-
North Dakota	-	-
South Dakota	1.22	-
South Atlantic		
Delaware	-	-
Florida	1.31	-
Georgia	1.50	-
Maryland	1.57	-
North Carolina	1.62	-
South Carolina	1.51	-
Virginia	1.52	1.37
West Virginia	1.62	1.62

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(1) "NR" indicates that value was not reported
(2) "-" indicates no production

TABLE 5 (Cont'd)

UNIT VALUE OF CRUSHED AND BROKEN LIMESTONE AND DOLOMITE IN THE UNITED STATES IN 1969, BY REGION AND STATE

Region and State	Average Unit Value ($/Ton)	
	Limestone	Dolomite
East South Central		
Alabama	1.17	1.60
Kentucky	1.46	-
Mississippi	1.00	-
Tennessee	1.33	-
West South Central		
Arkansas	1.36	-
Louisiana	-	-
Oklahoma	1.30	NR
Texas	1.35	1.17
Mountain		
Arizona	1.64	-
Colorado	2.04	2.83
Idaho	1.10	-
Montana	1.24	-
Nevada	1.64	1.77
New Mexico	1.51	NR
Utah	2.25	2.66
Wyoming	2.11	-
Pacific		
California	1.07	2.91
Oregon	1.00	-
Washington	1.28	6.00
Total United States	1.45	1.55

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(1) "NR" indicates that value was not reported
(2) "-" indicates no production

TABLE 6

DELIVERED PRICE OF HIGH-CALCIUM LIMESTONE TO SELECTED POWER PLANTS

Power Plant	Location	Delivered Price ($/Ton)
Benning	Washington, D.C.	4.50*
Gorgas	Gorgas, Alabama	3.23
Cherokee	Denver, Colorado	6.36
J. McDonough	Cobb County, Georgia	4.50
Devon	Millford, Connecticut	4.50*
Fisk	Chicago, Illinois	2.40
R.S. Wallace	East Peoria, Illinois	3.30
Will County	Lockport, Illinois	3.30
D.H. Mitchell	Gary, Indiana	2.65
Wabash	Terre Haute, Indiana	2.25 (75-94% $CaCO_3$)
Riverside	Iowana, Iowa	1.95
Lawrence	Lawrence, Kansas	3.66
Cane Run	Louisville, Kentucky	3.00
Elmer Smith	Owensboro, Kentucky	3.72
Riverside	Baltimore, Maryland	3.85
Edgar	N. Weymouth, Massachusetts	4.50*
L Street	Boston, Massachusetts	4.50*
Delray	Detroit, Michigan	2.40
High Bridge	St. Paul, Minnesota	3.00
Hawthorn	Kansas City, Missouri	4.60
Sioux.	West Alton, Missouri	3.10
Essex	Newark, New Jersey	4.50*
Port Jefferson	Port Jefferson, New York	4.50*
Waterside	New York, New York	4.50*
Allen	Belmont, North Carolina	5.39
Leland Olds	Stanton, North Dakota	13.20
Tidd	Brilliant, Ohio	3.80
Miami Fort	North Bend, Ohio	2.45
Acme	Toledo, Ohio	2.45
Horseshoe Lake	Horseshoe Lake, Oklahoma	8.00
Elrama	Elrama, Pennsylvania	5.55 (92% $CaCO_3$)
Schuylkill	Philadelphia, Pennsylvania	4.50*
Wateree	Rockland City, South Carolina	3.90 (88% $CaCO_3$)
Bull Run	Oak Ridge, Tennessee	4.24
Cabin Creek	Cabin Creek, West Virginia	6.00
Kammer	Captina, West Virginia	4.00 (80% $CaCO_3$)
Lakeside	St. Francis, Wisconsin	2.60

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* - Source of stone is outside of U.S. (Bahamas)

TABLE 7

AVAILABILITY OF LIMESTONE AND DOLOMITE FOR POLLUTION CONTROL (1969)

Region and State	Production (M Tons)	Potential Demand (M Tons)	Ratio
New England			
Connecticut	275	487	0.56
Maine	800	61	13.1
Massachusetts	750	636	1.18
New Hampshire	-	141	0
Rhode Island	< 100	39	< 2.56
Vermont	525	5	105
Totals	2,400	1,369	1.75
Middle Atlantic			
New Jersey	800	935	0.86
New York	33,457	2,132	15.7
Pennsylvania	56,667	3,516	16.1
Totals	90,900	6,583	13.8
South Atlantic			
Delaware	-	177	0
Florida	40,729	1,009	40.4
Georgia	4,334	931	4.66
Maryland	9,804	1,010	9.71
North Carolina	4,500	2,003	2.25
South Carolina	1,900	459	4.14
Virginia	17,829	1,088	16.4
West Virginia	8,405	1,794	4.69
Totals	87,500	8,471	10.3
East South Central			
Alabama	17,752	1,931	9.19
Kentucky	30,158	1,785	16.9
Mississippi	300	71	4.23
Tennessee	33,109	1,858	17.8
Totals	81,300	5,645	14.4
East North Central			
Illinois	54,844	3,665	15.0
Indiana	25,157	2,786	9.03
Michigan	39,066	2,511	15.6
Ohio	50,595	4,181	12.1
Wisconsin	15,937	1,164	13.7
Totals	185,600	14,307	13.0
West North Central			
Iowa	26,200	453	57.8
Kansas	15,334	42	365
Minnesota	4,127	648	6.37
Missouri	41,200	1,093	37.7
Nebraska	4,663	110	42.4
North Dakota	-	357	0
South Dakota	989	35	28.3
Totals	92,500	2,738	33.8

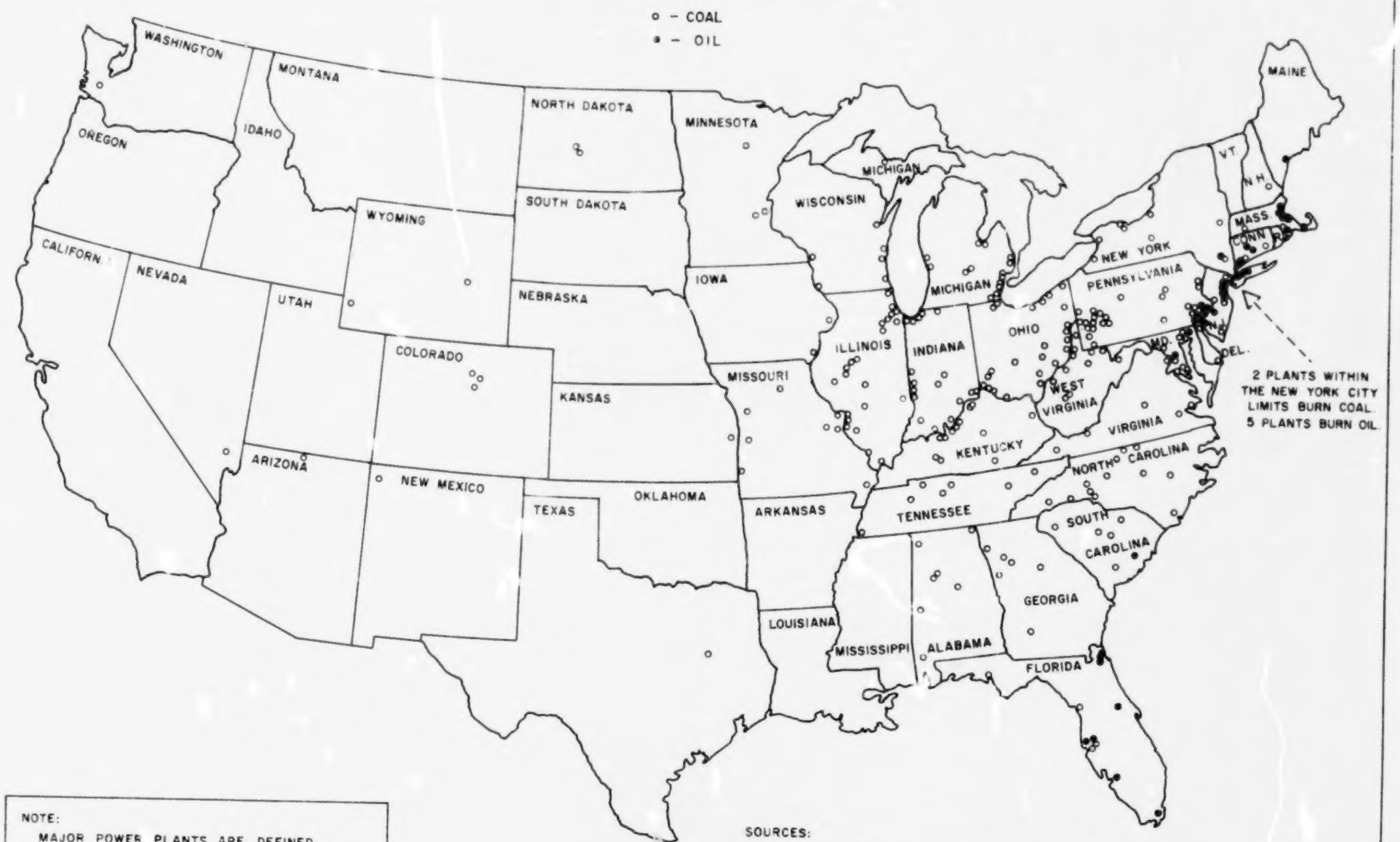
TABLE 7 (Cont'd)

AVAILABILITY OF LIMESTONE AND DOLOMITE FOR POLLUTION CONTROL (1969)

Region and State	Production (M Tons)	Potential Demand (M Tons)	Ratio
West South Central			
Arkansas	5,676	4	1419
Louisiana	-	<1	0
Oklahoma	16,300	< 1	Large
Texas	36,300	< 1	Large
Totals	58,300	< 7	Large
Mountain	2,339	50	46.8
Colorado	1,650	358	4.61
Idaho	250	-	∞
Montana	1,442	74	19.5
Nevada	1,000	78	12.8
New Mexico	956	345	2.77
Utah	2,400	67	35.8
Wyoming	649	379	1.71
Totals	10,700	1,351	7.92
Pacific			
California	17,400	266	65.4
Oregon	350	< 1	Large
Washington	1,050	< 1	Large
Totals	18,800	<268	>70

FIGURE 1

MAJOR THERMAL POWER PLANTS IN THE UNITED STATES BURNING COAL OR OIL AS THE PRIMARY FUEL



NOTE:
MAJOR POWER PLANTS ARE DEFINED AS THOSE HAVING INSTALLED GENERATING CAPACITIES OF 200 MEGAWATTS OR MORE.

SOURCES:
1. *Principal Electric Facilities*, Federal Power Commission, (1970). (Series of seven maps)
2. *Steam-Electric Plant Factors/1970 Edition*, National Coal Association, Washington, D.C., (November 1970).

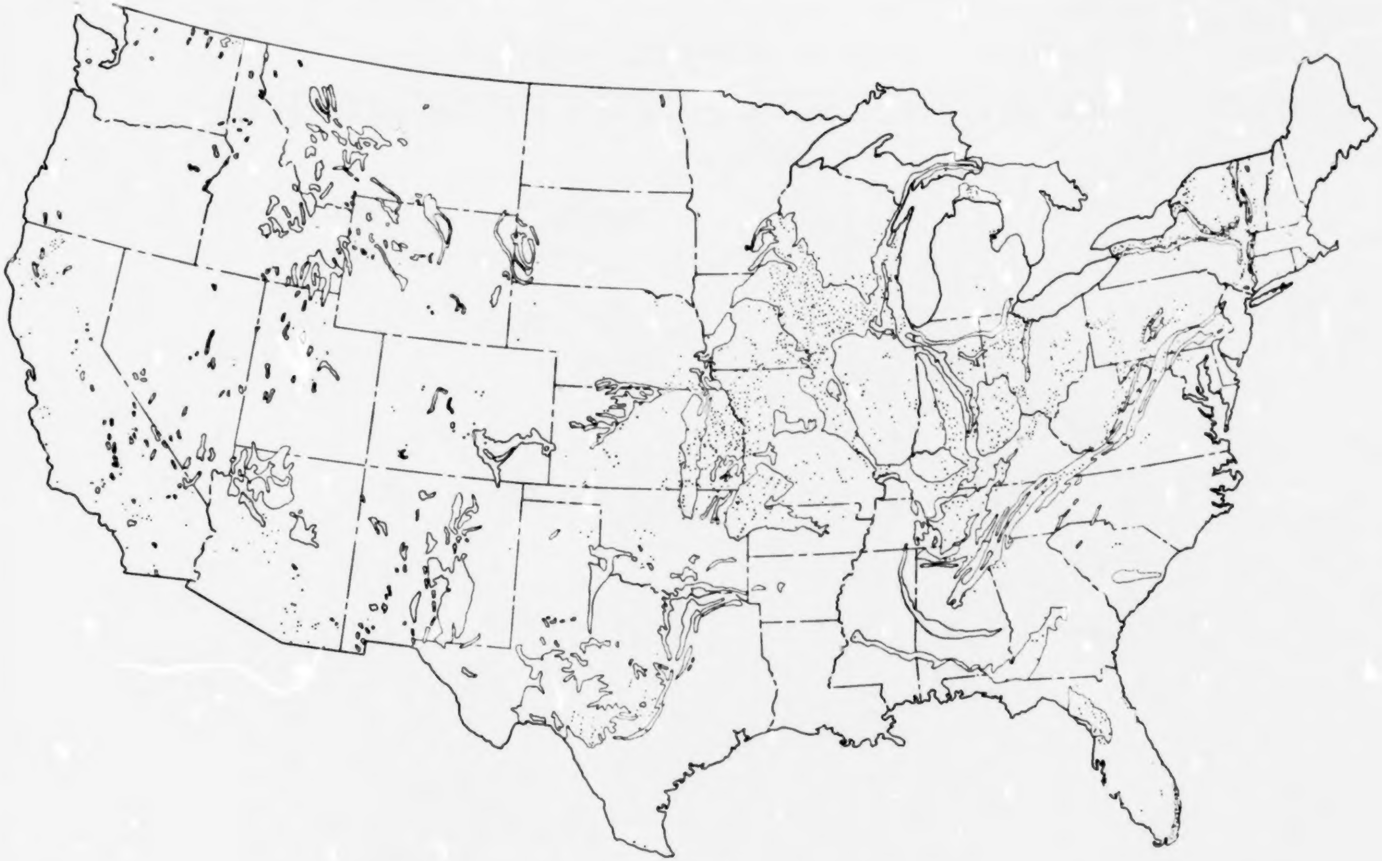


FIGURE 2

CARBONATE ROCK DEPOSITS IN THE UNITED STATES

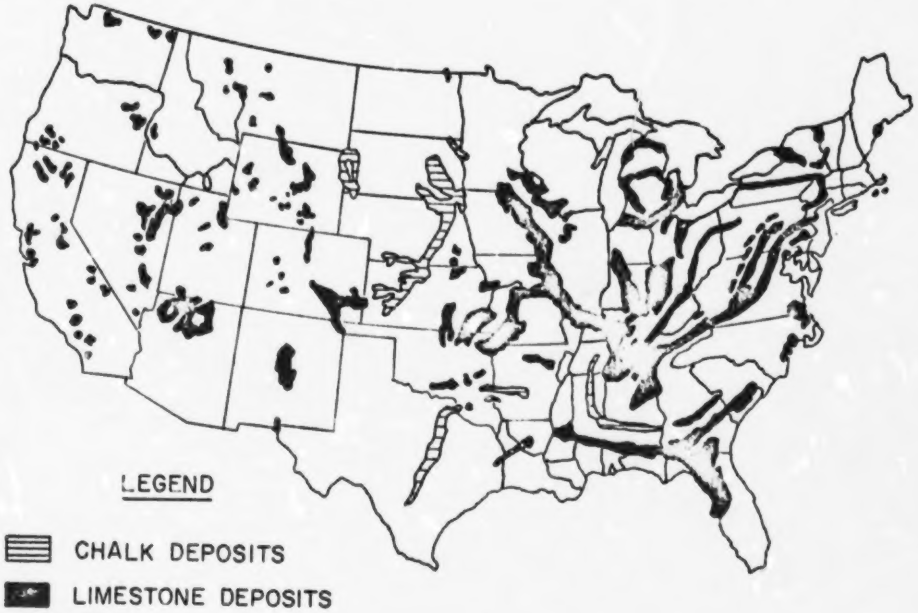


FIGURE 3

DISTRIBUTION OF CHALK AND LIMESTONE DEPOSITS IN THE UNITED STATES

(REPRINTED FROM U.S. BUREAU OF MINES BULLETIN NO. 395)

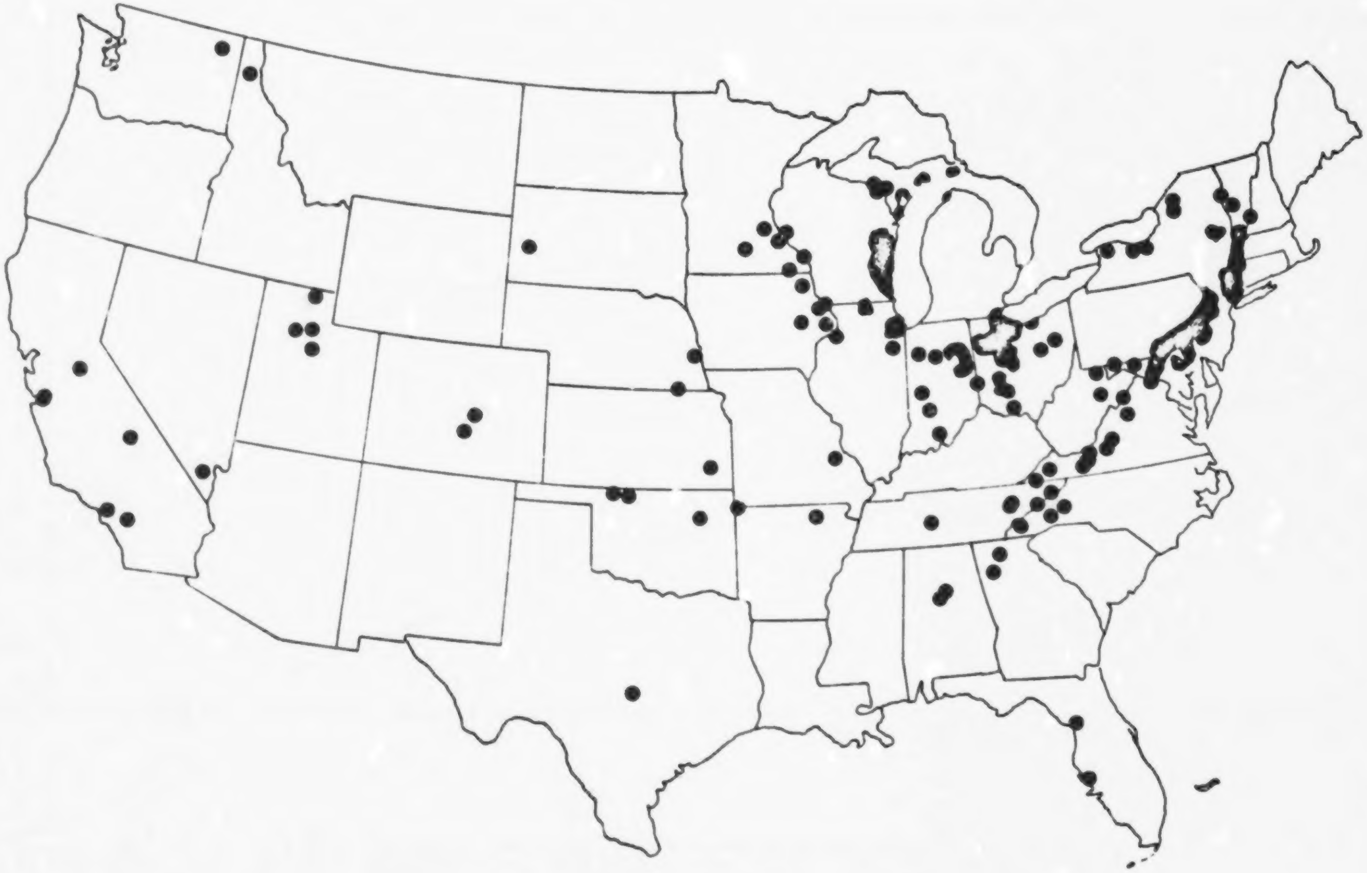


FIGURE 4

LOCATION OF HIGH-GRADE DOLOMITE QUARRIES IN THE UNITED STATES

(REPRINTED FROM U.S. BUREAU OF MINES INFORMATION CIRCULAR NO. 7192)

FIGURE 5
TRUCK TRANSPORTATION RATES FOR SHIPMENTS OF CRUSHED STONE IN THE UNITED STATES

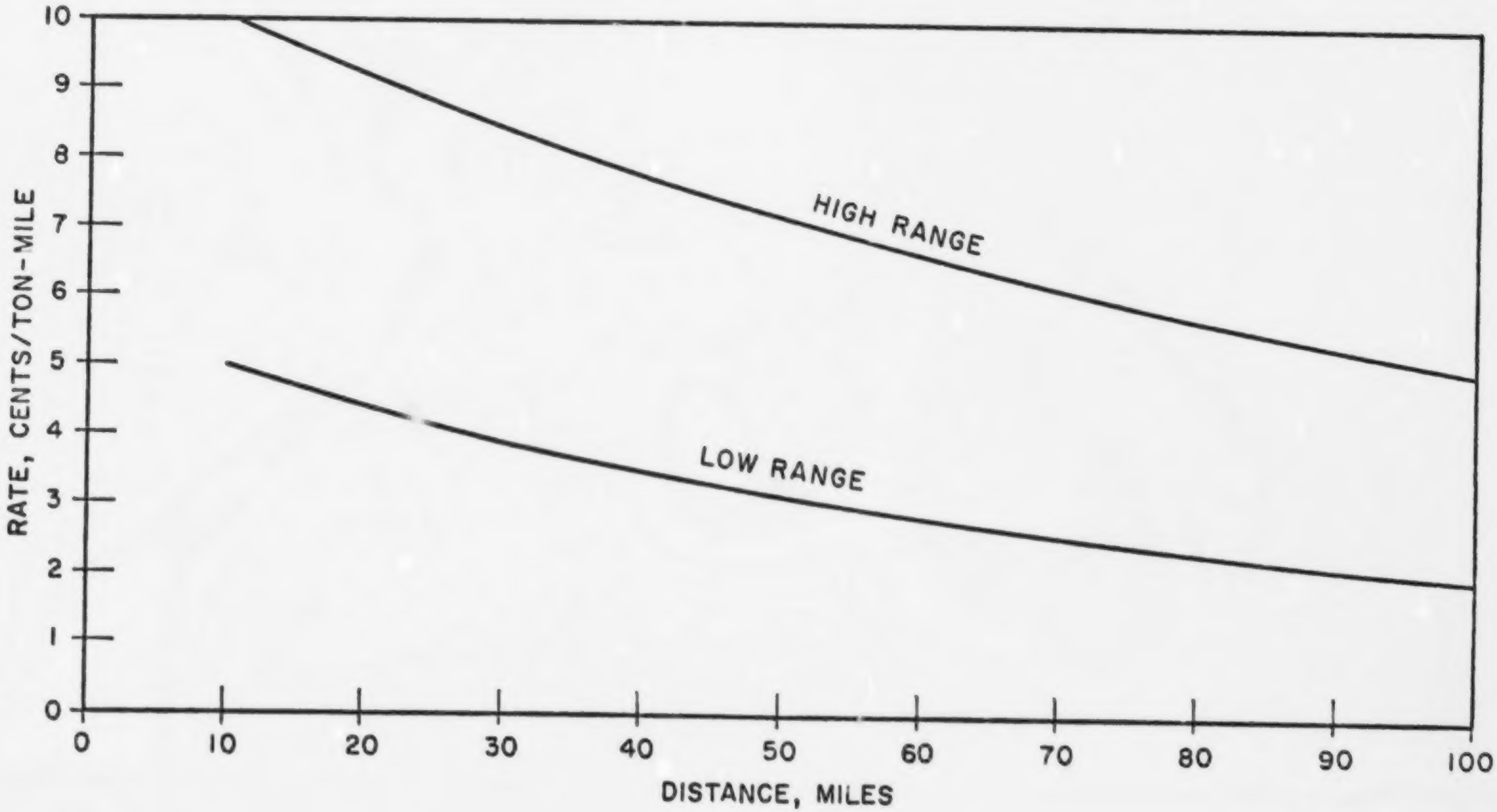


FIGURE 6

RAIL TRANSPORTATION RATES FOR SHIPMENT OF CRUSHED STONE IN THE UNITED STATES

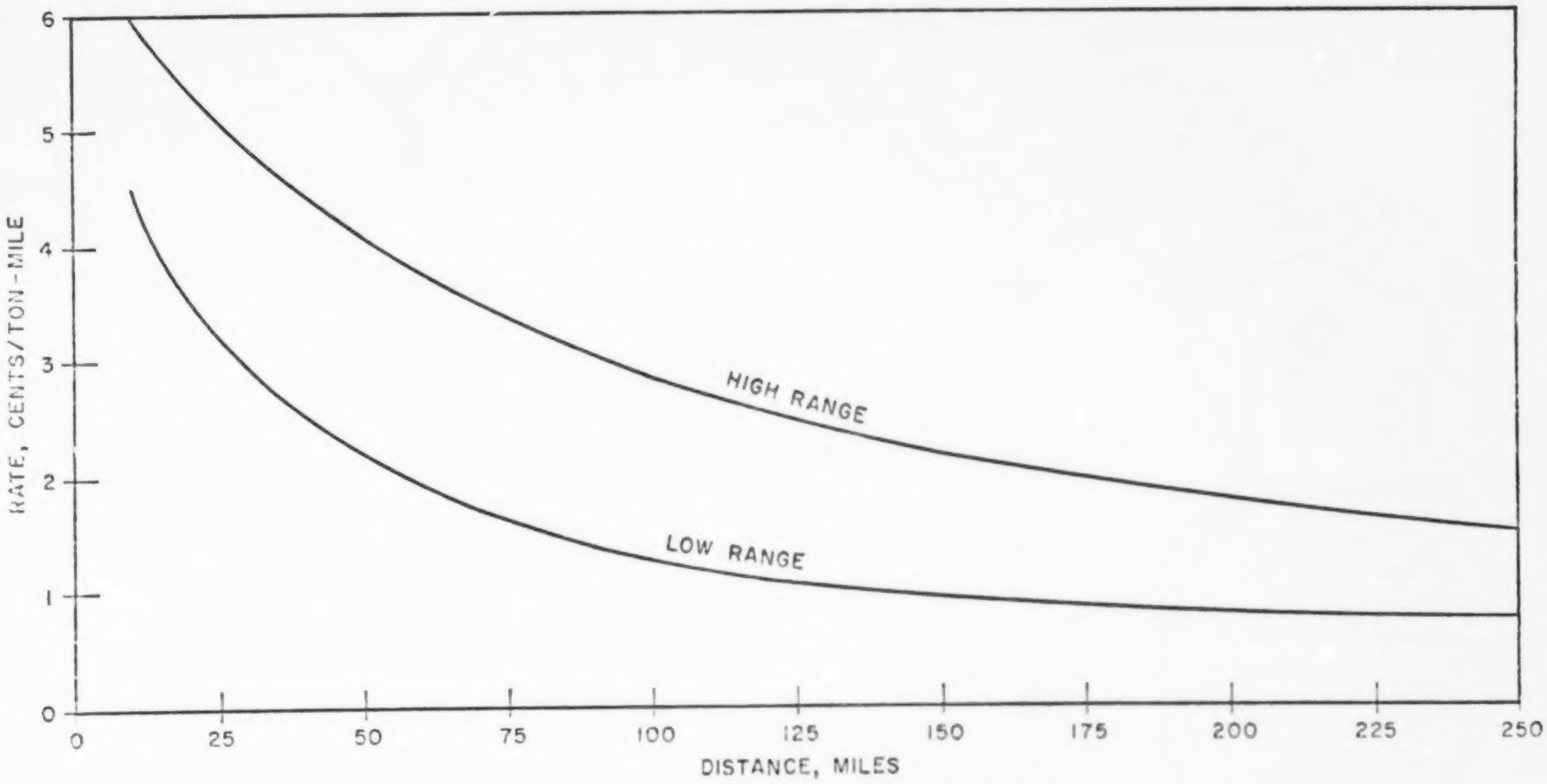
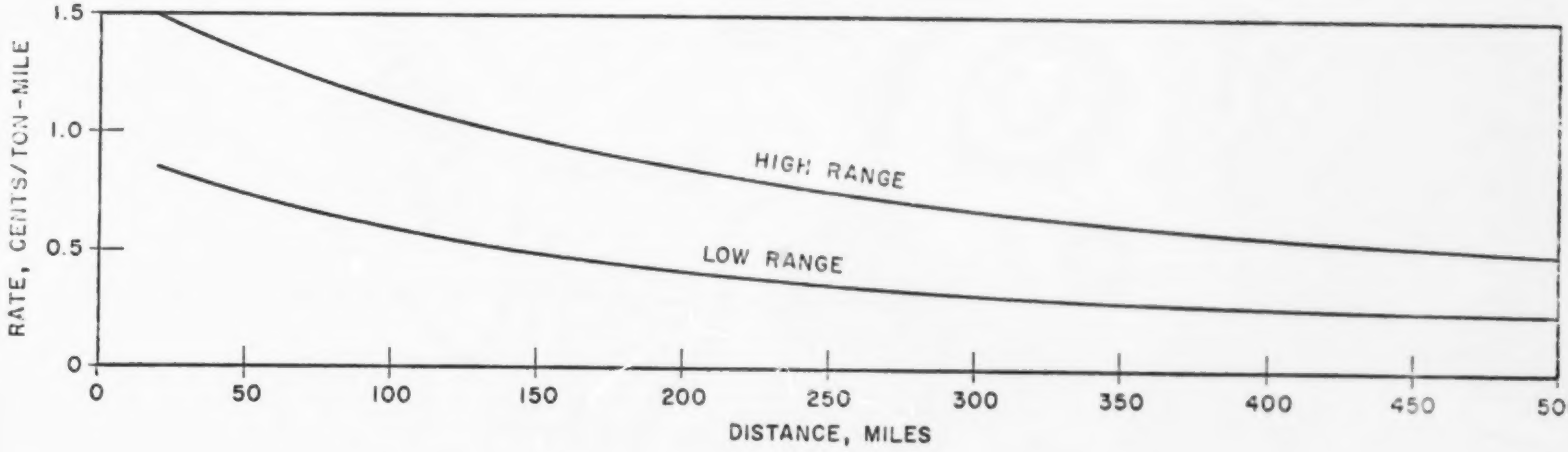


FIGURE 7

WATERWAY TRANSPORTATION RATES FOR SHIPMENT OF CRUSHED STONE IN THE UNITED STATES



THE PILOT SCALE R&D AND PROTOTYPE PLANT OF MHI LIME-GYPSUM PROCESS

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Office of Air Program, Division of Control System
Sheraton-Charles Hotel, New Orleans, Louisiana

8 - 12 November, 1971

THE PILOT SCALE R&D AND PROTOTYPE PLANT OF MHI LIME-GYPSUM PROCESS

Tsukumo Uno, Dr. *
Masumi Atsukawa **
Kenzo Muramatsu **

ABSTRACT

The lime-gypsum process is a method in which flue gas is scrubbed with lime slurry to remove SO_2 and gypsum is recovered as byproduct through air oxidation of calcium sulfite formed in the absorber. This process has been attracting particular attention as an advantageous desulfurization process in Japan because of its remarkable features - abundant and cheap absorbent, large demand for by-product gypsum, no waste to be thrown away, simple desulfurization system, etc.

The technical feasibility is already proved by the six years operation record of 62,500 Nm^3/hr plant which was constructed for a sulfuric acid plant by our company under the license of Japan Engineering and Consulting Co. We have conducted recently a pilot scale research and development on this process to make the process fit to the treatment of flue gas from an oil firing boiler. On the basis of the test results, a prototype plant, treating 100,000 Nm^3/hr flue gas is under construction at a power station. Here description is made shortly on the results of the pilot test and outline of the plant.

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INTRODUCTION

We have been conducting research and development of a lime/limestone scrubbing process since about ten years ago. In 1962 - 1963, we carried out a pilot test at Amagasaki No.3 P/S, Kansai Electric Power Co. which treats 5,400 Nm^3/hr flue gas from an oil firing boiler. Through this pilot test, we have obtained technical data on gas cooling and carbon dust removal by means of a spray tower and on the SO_2 removal by means of various types of scrubbers. In 1964 was constructed the first commercial lime-gypsum plant treating waste gas from sulfuric acid plant at Koyasu works, Nippon Kokan Co. This plant has been working smoothly for about six years producing high quality byproduct gypsum for sales on the market.

Though the technical feasibility of the lime-gypsum process has proved that it can treat waste gas from sulfuric acid plant as aforementioned, application of the process to the power plant includes some problems to be solved. That is, we have to overcome difficulties due to the differences of the characteristics of these plants as shown in Table 1. This paper describes shortly the results of pilot tests which have been carried out to solve these problems as mentioned hereunder and an outline of the prototype plant being under construction at Amahigashi P/S, Kansai Electric Co.

(1) How to design an economical and efficient scrubber suitable for treating a large volume of flue gas with lime slurry.

(2) How to prevent the plugging due to deposition of sludge and occurrence of hard gypsum scale.

(3) How to obtain high quality gypsum without the influence of impurities from flue gas and in raw materials.

(4) How to satisfy both high SO_2 removal and high Ca reactivity in case thin SO_2 is to be treated.

OUTLINE OF MHI LIME-GYPSUM PROCESS

Though the process differs somewhat depending on conditions of waste gases to be treated hereby, it consists of the following sections basically as shown in Fig. 1.

(1) Gas cooling and dust removal section

This is a section to clean, moistened and cool flue gas with water before the gas is sent to absorbers.

(2) Absorption section

This is a section in which oxides of sulfur are absorbed by lime slurry.

$$Ca(OH)_2 + SO_2 + Aq = CaSO_3\cdot\frac{1}{2}H_2O + Aq \qquad (1)$$

$$Ca(OH)_2 + SO_3 + Aq = CaSO_4\cdot 2H_2O + Aq \qquad (2)$$

$$CaCO_2 + SO_2 + Aq = CaSO_3\cdot\frac{1}{2}H_2O + CO_2 + Aq \qquad (3)$$

$$CaCO_3 + SO_3 + Aq = CaSO_4\cdot 2H_2O + CO_2 + Aq \qquad (4)$$

$$Ca(OH)_2 + CO_2 + Aq = CaCO_3 + Aq \qquad (5)$$

$$CaSO_3\cdot\frac{1}{2}H_2O + \frac{1}{2}O_2 + Aq = CaSO_4\cdot 2H_2O + Aq \qquad (6)$$

The main reaction of SO_2 absorption produces calcium sulfite as seen in equations (1) and (3) and some amount of calcium sulfate is also produced depending upon SO_3 and O_2 contents of the flue gas and operating conditions of absorber as seen in equations (2), (4) and (6).

(3) pH value adjusting section

The pH value of the spent liquor from the absorption section is adjusted here to 4 - 4.5 by adding a small amount of sulfuric acid.

(4) Oxidating section

This is the section of converting calcium sulfite to gypsum by air oxidation at 4 - 5 kg/cm^{2}G.

(5) Gypsum filtering section

Gypsum is filtered out of the slurry delivered from the oxidation tower. The filtrate is fed back to the cooling tower.

(6) Impurities separating section

The impurities brought with flue gas or raw materials (lime) are separated out of the system by neutralizing the waste water of the cooling tower with slaked lime and filtering this liquor.
The filtrate is fed back to the process.

PILOT SCALE RESEARCH AND DEVELOPMENT

The photographs of the pilot plant at which the tests on the MHI lime-gypsum process have been conducted are shown in Fig. 2 and 3. This plant was designed to be able to produce 0.7 T/D of gypsum by treating 2,000 - 3,000 Nm^3/hr of flue gas and installed at Hiroshima Technical Institute in October 1969. The test results are as follows.

1. Selection of the scrubber type - economical, efficient and free from scaling

As they well know. the prevention of scaling trouble is the most important problem at the designing of lime/limestone scrubbers.
From this standpoint, we adopted a spray tower as a scrubber of simple structure for the treatment of waste gas from sulfuric acid. In this case, the application of this process is rather easy because the amount of gas is rather small and also it has higher SO_2 content, negligible amount of CO_2 and no particulates.

To apply this process to other sorts of plant as shown in Table 1, we have carried out a series of pilot test and found that the plastic grid packed tower is suitable to the process ~~at~~ as it can be operated without scaling trouble at a higher superficial gas velocity and lower draft pressure loss. For the flue gas containing 0.1 vol % of SO_2, 90 to 98 % of SO_2 removal is attainable at a superficial gas velocity of about 1.2 x 10^4 $m^3/m^2 \cdot hr$ and a total draft pressure loss about 90 mmH_2O. The flow rate of scrubbing liquor is 70 m^3/m^2 hr. in this case.

2. Reaction rate in the scrubber

The absorption reaction occurred in the scrubber is mainly controlled by the dissolving rate of lime as shown in Fig. 5 and the dimension of the scrubber can be determined by the equation (1) and (2).

$$\log \frac{Y_{in}}{Y_{out}} = K\alpha \cdot C_O P_O \cdot (1 - \eta) \cdot \frac{Z}{G'} \qquad (1)$$

$$K\alpha = A \cdot {C_O}^{a} \cdot (L/G)^{b} \qquad (2)$$

From these equations and Fig. 4 and 6, it is clear that a higher pH value is requested together with a higher liquid-gas ratio for attaining a higher absorption efficiency. However, a lower pH value is necessary for attaining a high conversion ratio of lime to calcium sulfite or sulfate (this is designated here as Ca reactivity). To accommodate these conflicting factors, we have adopted two scrubbers combined system in which one is operated at a lower pH and the other at a high pH.
The two scrubbers are installed in series in relation to gas stream - the former is countercurrent and the latter is cocurrent. The scrubbing liquor is at first fed to the latter and the effluent is then sent to the former. The volume of each scrubber necessary for 90 % SO_2 removal and 98 % Ca reactivity is related with pH value of the latter scrubber, as shown in Fig. 7. This figure shows that the most economical point exists at the pH value of 9, but practically we have to use a lower pH at which the formation of calcium carbonate is not predominant in the scrubber

when carbon dioxide content is high in the gas to be treated.

3. Prevention of plugging in the scrubber

Troubles often encountered in the lime scrubbing process are the accumulation of soft deposit and the formation of hard scale in the scrubber. The former is usually caused by the deposition of calcium carbonate or sulfite and it is preventable by operating the scrubber at a suitable pH and avoiding the stagnant portion in the scrubber. The latter is caused by the growth of gypsum crystals and then the desupersaturation of scrubbing liquor is the most effective countermeasure for the scaling. For this purpose, addition of the seed crystals and installation of the delay pipe are well known. And also to avoid stagnant flow or portions dried intermittently in the scrubber is very important because the crystalline scale of gypsum often begins to grow by concentration of the liquid at these portions. We have realized all of these countermeasures at the pilot test and found no sign of scaling after a 500 hours continuous operation.

4. Oxidation of calcium sulfite

The oxidation of calcium sulfite is conducted in a tower equipped with the rotating cylinder type of air atomizer at 4 - 5 kg/cm2 and 50 - 80°C. The principle and features of this specially devised atomizer were explained at the first symposium. However, we like to again emphasize that this may be the most suitable one for the lime-gypsum process as it is operated at a very high oxidation efficiency without fear of plugging.

The rate of oxidation depends on pH value of the slurry as shown in Fig. 8 and we adopt pH 4 - 4.5 at practical operation. This figure suggests us that HSO_3 ion in the slurry may take an important role in the oxidation reaction. The seed crystal added in the scrubbing liquor serves again for the growth of gypsum crystals.

OUTLINE OF A PROTOTYPE PLANT

A prototype plant of MHI lime-gypsum process treating 100,000 Nm^3/hr of flue gas from an oil firing boiler is under construction at Amahigashi P/S, Kansai Electric Power Company. This plant is designed to remove 90 % of SO_2 from flue gas containing 0.11 vol % SO_2 and produce daily 19 tons of gypsum for sales in which quick lime is used as absorbent. It is scheduled to be completed in March 1972 and operated for about one year after the guarantee run to confirm such problems as concerned with materials of construction, quality of byproduct, performance characteristics and economics through the long run. The production/demand of gypsum and distribution of limestone in Japan are shown in Fig. 9 and 10 respectively.

SUMMARY

The lime-gypsum has been attracting particular attention in Japan as an advantageous desulfurization process because it produces gypsum which has a great possible share in the market by the simple process using lime as absorbent which is cheap and abundant in Japan. Here described are the test results on the process at the pilot plant treating 2,000 Nm^3/hr of flue gas from an oil firing boiler, especially on the rate of absorption reaction and the techniques for prevention of scaling. The technical feasibility and economics of this process will be made clear through the operation of the proto-

type plant which will be started to operate in March 1972.

NOTATION

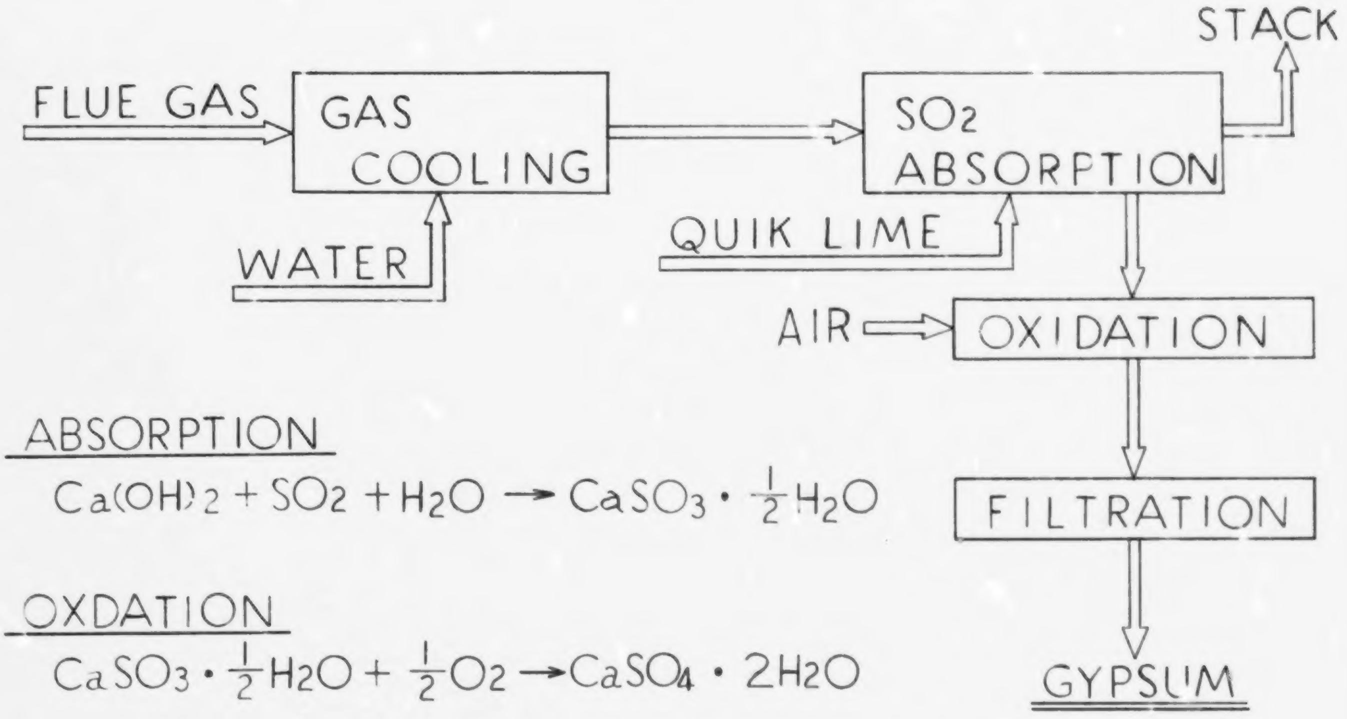
Y_{in}, Y_{out}	SO_2 concentration at the inlet and outlet of the scrubber, respectively	ppm
P_o	Pressure of gas in the scrubber	atm
C_o	Effective concentration of Ca in slurry	kg-mol/m^3
η	Ca reactivity	-
Z	Effective height of scrubber	m
G'	Molar superficial gas velocity in the scrubber	kg-mol/m2.hr
K_a	Mass transfer coefficient based on dissolving of Ca	1/hr.atm

CONDITIONS OF FLUE GAS FROM SEVERAL SORTS OF PLANT

(TABLE 1)

	SULFURIC ACID PLANT	PETROLEUM REFINERY PLANT FURNACE	OIL FIRING POWER PLANT	SINTERING MACHINE FOR STEEL PRODUCTION
GAS QUANTITY ($10^3 \times Nm^3/H$)	50 ~ 100	100 ~ 200	500 ~ 3000	500 ~ 2000
TEMPERATURE (°C)	80 ~ 95	200 ~ 300	130 ~ 145	70 ~ 300
DUST QUANTITY (g/Nm^3)	0	0.1	0.1 ~ 0.2	0.5 ~ 3.0
GAS COMPOSITION (VoL %)				
$SO_2 + SO_3$	0.1 ~ 0.3	0.13	0.08 ~ 0.13	0.02 ~ 0.12
O_2	6 ~ 7	8.4	3 ~ 4.5	10 ~ 20
CO_2	0	6.8	11 ~ 12	4 ~ 13
H_2O	0	7.3	10 ~ 11	9 ~ 11

Fig-1 MHI LIME-GYPSUM PROCESS



ABSORPTION

$$Ca(OH)_2 + SO_2 + H_2O \rightarrow CaSO_3 \cdot \frac{1}{2}H_2O$$

OXDATION

$$CaSO_3 \cdot \frac{1}{2}H_2O + \frac{1}{2}O_2 \rightarrow CaSO_4 \cdot 2H_2O$$

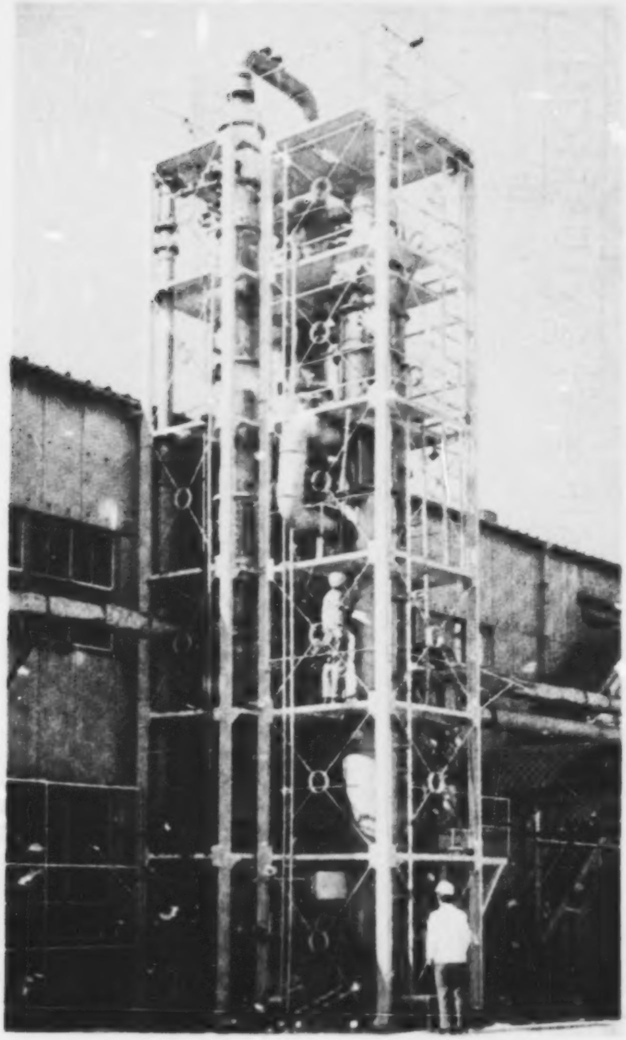


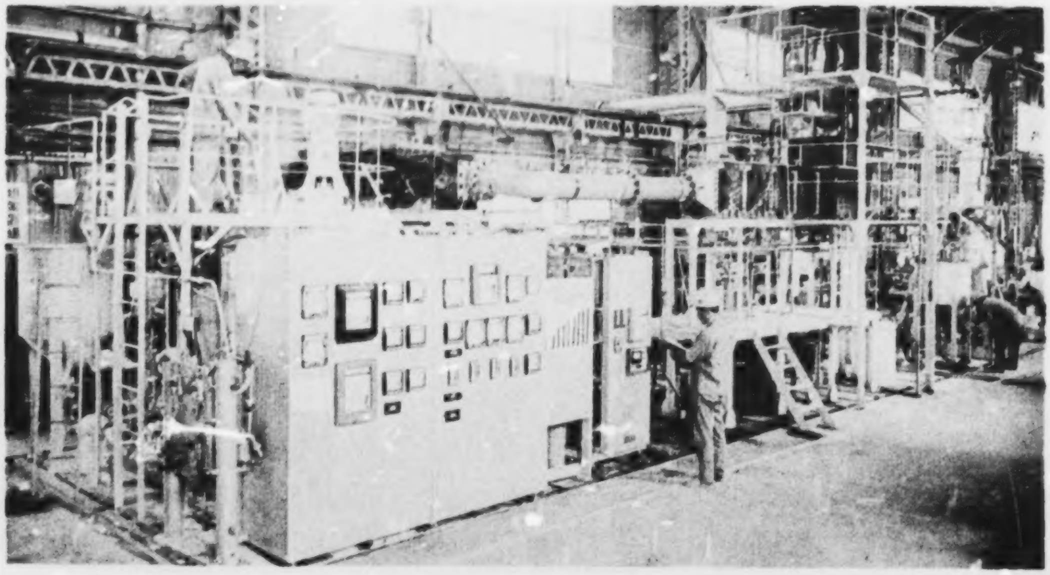
Fig. 2 (left)

Photograph of the scrubbers at which pilot tests have conducted on the lime-gypsum process.

Fig. 3 (under)

Photograph of the pilot plant besides the scrubbers at which the tests have conducted on the lime-gypsum process.

This picture shows inside of the house which is seen in the Fig. 2.



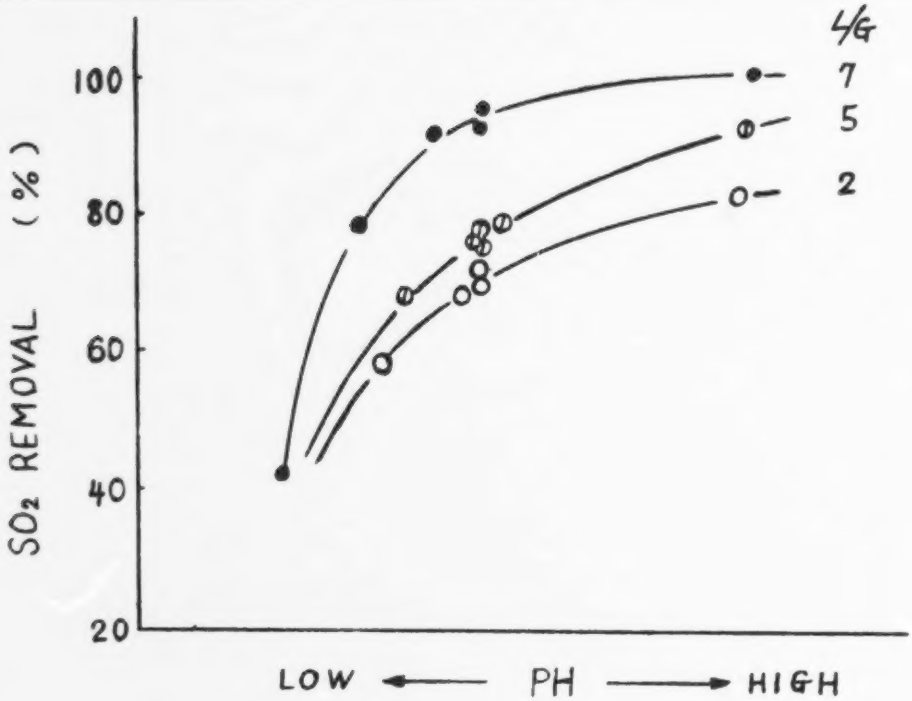


Fig. 4 – SO_2 REMOVAL/OPERATING CONDITION

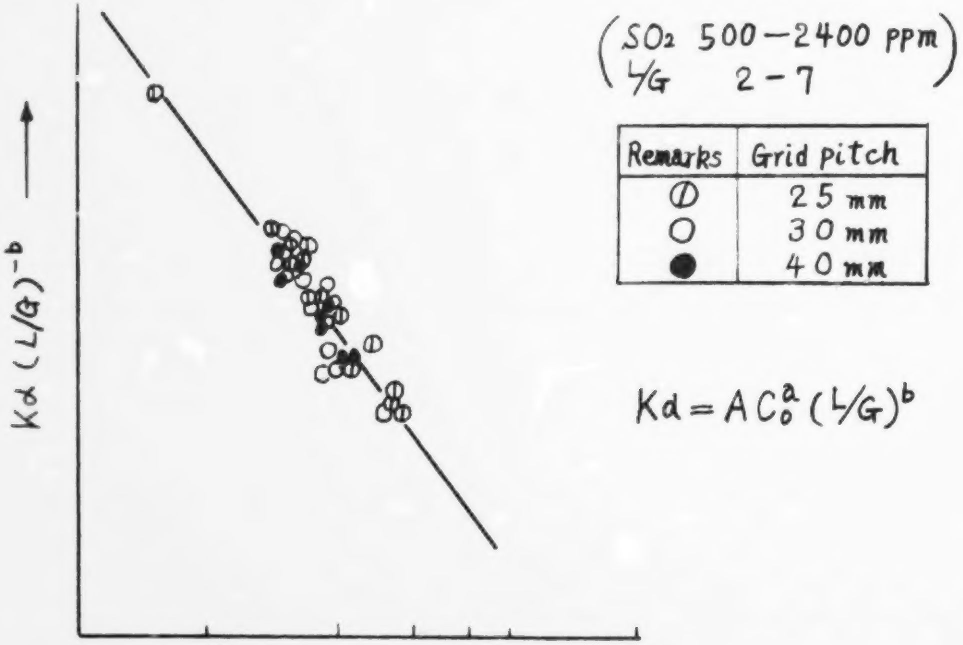


Fig. 5 – RATE OF ABSORPTION REACTION

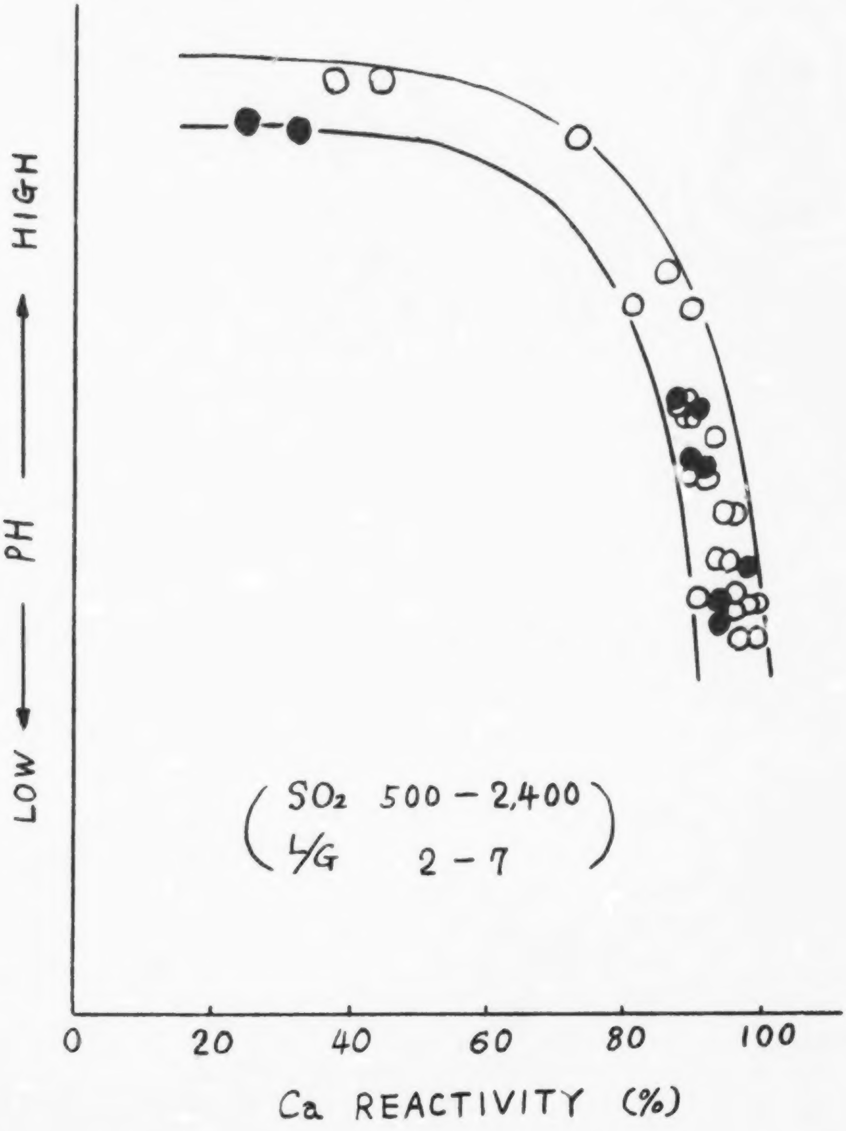


Fig.6 EFFECT OF PH ON Ca REACTIVITY

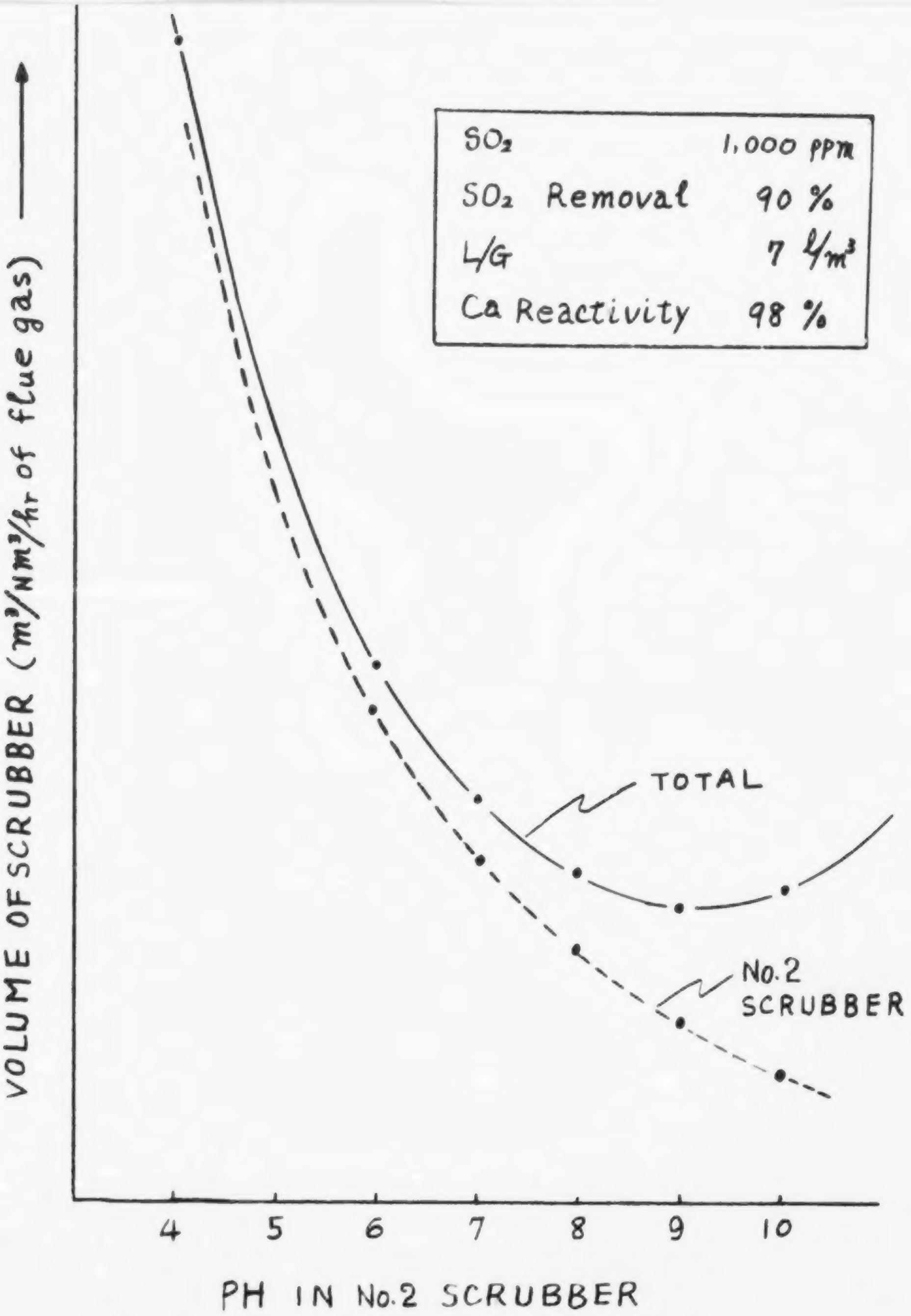


Fig. 7 RELATION – SCRUBBER VOLUME/PH IN No.2

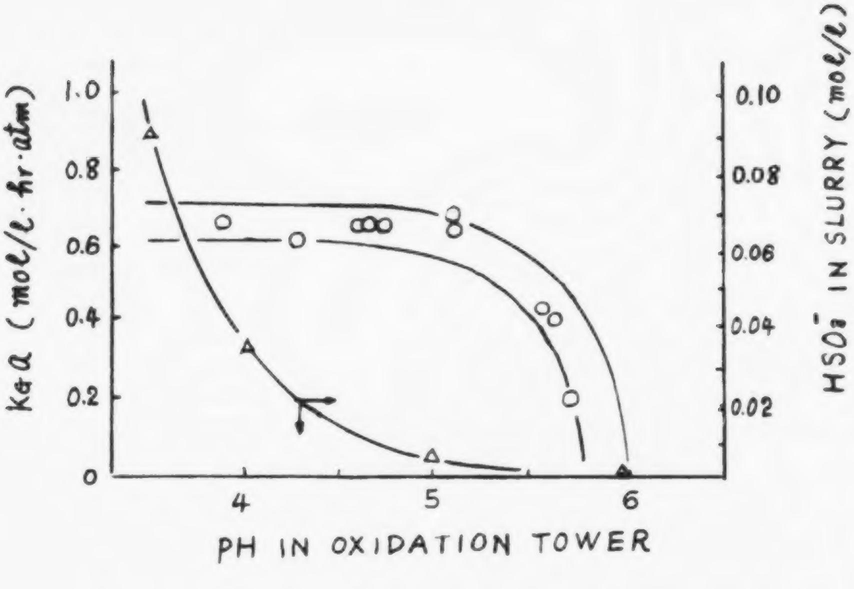


Fig. 8 EFFECT OF PH ON OXIDATION RATE

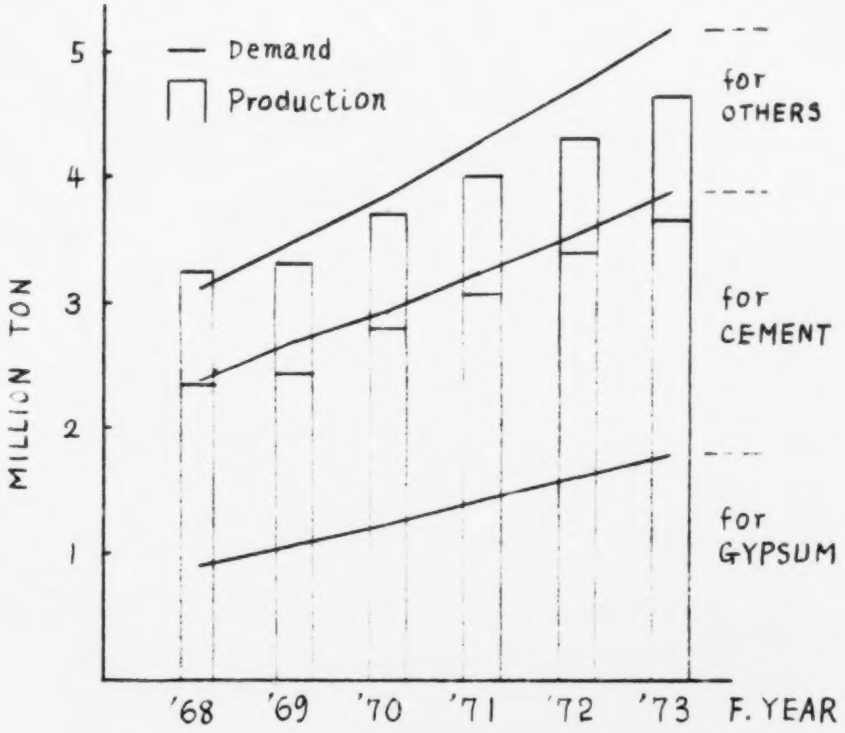
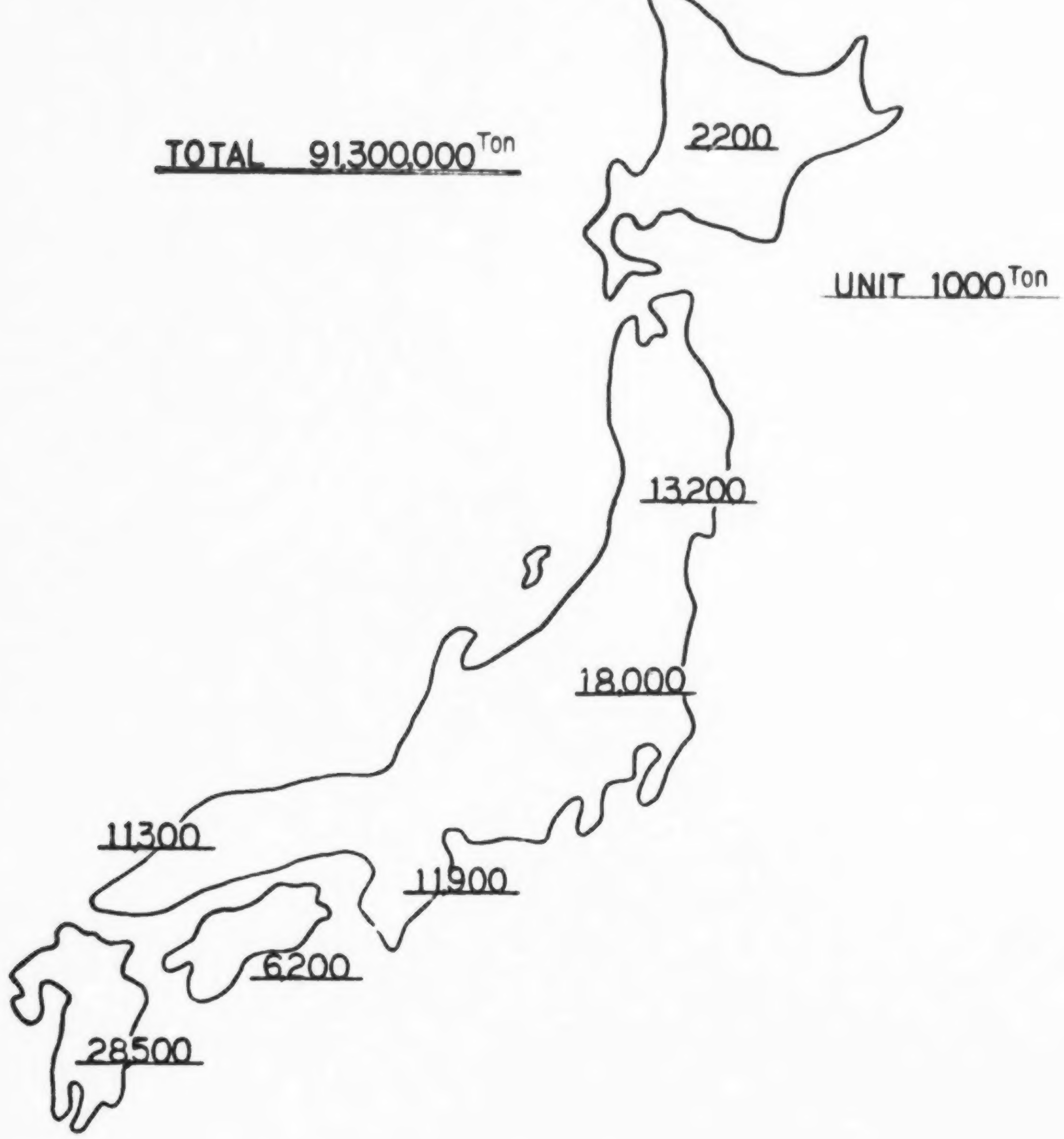


Fig. 9 PRODUCTION/DEMAND OF GYPSUM
IN JAPAN

LIME STONE. PRODUCTION CHART (1969)

(Fig. 10)



WET SCRUBBER INSTALLATIONS
AT
ARIZONA PUBLIC SERVICE COMPANY
POWER PLANTS

PRESENTED BY:

LYMAN K. MUNDTH

VICE PRESIDENT, POWER PRODUCTION
ARIZONA PUBLIC SERVICE COMPANY
PHOENIX, ARIZONA

PRESENTED AT:

INTERNATIONAL
LIME / LIMESTONE WET SCRUBBING SYMPOSIUM
SPONSORED BY DIVISION OF CONTROL SYSTEMS
U. S. ENVIRONMENTAL PROTECTION AGENCY
NEW ORLEANS, LOUISIANA
NOVEMBER 8 - 12, 1971

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WET SCRUBBER INSTALLATIONS
AT ARIZONA PUBLIC SERVICE COMPANY
POWER PLANTS

INTRODUCTION

Arizona Public Service Company is pioneering the installation of wet flue gas scrubbing equipment on coal fired power plants with work currently progressing at two of its operating stations, one in New Mexico and the other in Arizona.

At the Four Corners Plant, near Farmington, New Mexico, scrubbers are being installed on three units with a total net generating capacity of 575 MW (nominal).

The other installation is at the Cholla Power Plant at Joseph City, Arizona, a single unit, with a rating of 115 MW (nominal).

The Four Corners Plant is fueled with sub-bituminus coal from the Navajo Mine which is adjacent to the plant. This coal has a high ash content; ranging from 6 to 25%, and averages about 22%. The coal has a low sulfur content; with a range of 0.4 to 1.9% and averages about 0.7%.

The Cholla Plant coal is from the McKinley Mine at Gallup, New Mexico. The ash content varies from 5 to 15%, with an average of about 8%. The sulfur content is from 0.4 to 1.0% with an average of about 0.5%.

I. EQUIPMENT CONCEPT

At the time this report was prepared both the state of New Mexico and Arizona had particulate emission regulations, but neither state had adopted SO_2 emission limits for power plants. However, both states are currently in the process of adopting SO_2 emission regulations.

The wet scrubber concept of cleaning flue gases was selected because of concern for the effectiveness of electrostatic precipitators with low sulfur coal and for the SO_2 removal capabilities of the scrubbers.

A. Four Corners Plant The scrubber installation at the Four Corners Plant is being performed by the Chemical Construction Company (CHEMICO) and will use Chemico's variable throat, high energy, wet approach venturi for particulate removal. A pilot plant test has been conducted to obtain design data and operating parameters for the scrubber system.

B. Cholla Plant The Cholla installation has been awarded to Research-Cottrell, Inc. for design and construction and will use a high energy, flooded-disc venturi for particulate removal and an absorber tower following the venturi for SO_2 removal. A 5000 CFM pilot plant is presently being installed to optimize recycle rates, verify materials of construction, and to conduct various chemical control tests.

II. ADDITIVE ABSORBER

Neither plant has a completely engineered SO_2 removal system at the present time, although the basic concepts of SO_2 removal have been studied and provisions are being incorporated.

A. Four Corners Pilot plant tests conducted at the Four Corners Plant by Chemico demonstrated that approximately 10 to 20% SO_2 removal occurs simultaneously with particulate removal in the venturi. The capability exists for further SO_2 removal by injecting supplementary sprays, after the venturi, in the lower section of the scrubber vessel and appropriate connections are being provided at this time for these sprays.

B. Cholla Plant In the Cholla scrubber, SO_2 removal will take place in a second stage, utilizing a wetted film, fixed packing absorber tower with an alkaline solution as the absorption medium.

III. PROCESS CONFIGURATION

Both the Four Corners and the Cholla scrubber systems will employ a continuous loop scrubbing cycle with part of the cycle liquor bled-off to continuously agitated thickeners. The clarified water will be returned to the scrubbing cycle for make-up.

Both installations provide for reheat of the flue gas before entering the stack to minimize negative bouyancy effects of the plume and to prevent condensation of the flue gas within the stack.

Both scrubber installations are retrofits to existing plants with the major part of the construction taking place with the units in service.

A. Four Corners Plant At Four Corners, space is limited. The venturi scrubber vessels (two venturi scrubber vessels on each unit) have been mounted above the existing mechanical dust collectors and induced draft fans. The particular arrangement was dictated because of limited construction space and priority of continuous plant operation during the scrubber installation. With two scrubbers on each unit, and appropriate ducting and baffles, the unit will be able to operate at 50% load if one of the scrubbers is out of service for repairs or maintenance.

New induced draft fans will be placed downstream from the scrubbers, and designed to handle the wet gas. The fans will have stainless steel rotors and rubber lined casings. The fans will discharge into mist eliminators which will help reduce the flue gas reheat requirements by drying the flue gas before it enters the reheater.

B. Cholla Plant At the Cholla Plant, the existing mechanical dust collectors and induced draft fans will be retained. The new scrubber system will be installed in series with, and downstream from the existing mechanical collectors and I. D. fans. New booster fans are required to operate in series with each of the existing induced draft fans to satisfy the additional pressure drop requirements of the scrubber system. More construction space is available at this site, and the scrubbers will be installed at ground level. Again, two scrubbers will be installed to provide the capability of half load operation when one scrubber is out of service.

IV. WASTE DISPOSAL

At both plants it is planned that the concentrated solids (fly ash and sulfates and sulfites of calcium) in the thickener under-flow will be transported to the existing plant ash disposal area in a separate transport system. Presently, wet sluice systems transport the fly ash to retention ponds.

V. PRESENT STATUS OF CONSTRUCTION

Construction and installation of the Four Corners scrubbers is nearly complete. The scrubbers are scheduled to be in operation by December, 31 of this year (1971). These scrubbers will be "tied-in" during scheduled maintenance outages continuing through the latter part of this month (November) and into December.

The Cholla scrubber is scheduled to be in operation by December 31, 1972. The design work and materials procurement is currently in progress. The pilot plant is being installed at the plant at the present time, and scheduled to be operating after the first of the year.

VI. DESIGN CONSIDERATIONS

The nature of an electric utility requires a very high degree of reliability in its generating facilities. The installation of largely untried and commercially unproven pollution control equipment will most certainly degrade the reliability of the generating units on which it is installed. Consequently, an extreme amount of care must be taken in the design and selection of wet scrubbers, or any other SO_2 removal equipment to maintain this high degree of reliability. Specific items to be considered are:

1. Redundancy of Critical Equipment Because emission regulations will, in most cases, prohibit the operation of generating units without the pollution control equipment in service, the same redundancy is required in the design of this equipment as is used

throughout the rest of the plant. This means that for any critical piece of equipment, a spare should be installed with provisions for on-line isolation and repair.

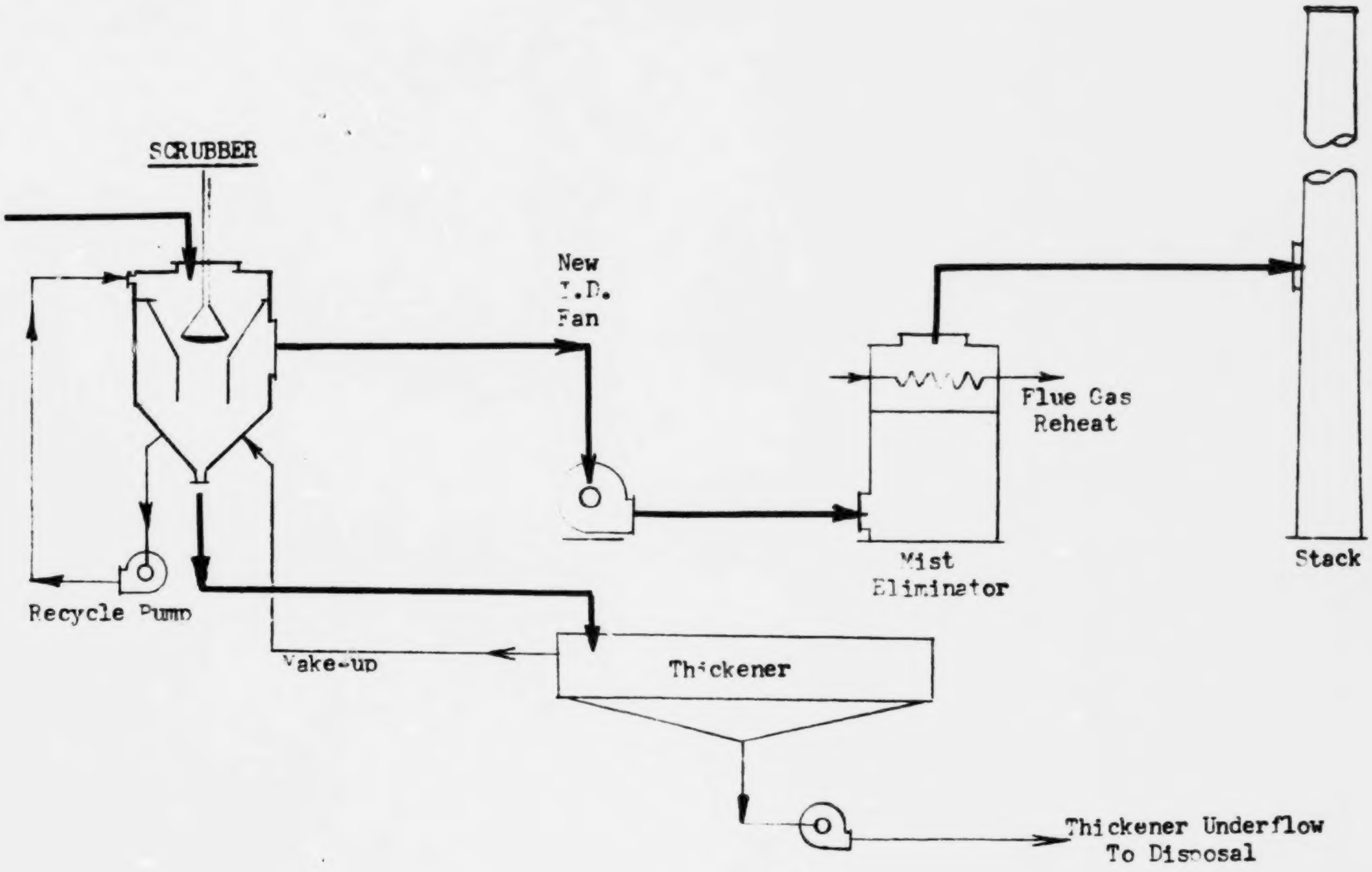
2. Controls The Controls, and the control system philosophy of the removal system must be compatible with, and integrated into, the control system for the rest of the plant.

3. Plant Personnel Plant personnel must be trained in the operation and maintenance of the removal equipment.

4. Materials Careful specification of materials of construction is required throughout and each component of the removal system must be individually studied to determine the severity of duty to which it will be subjected.

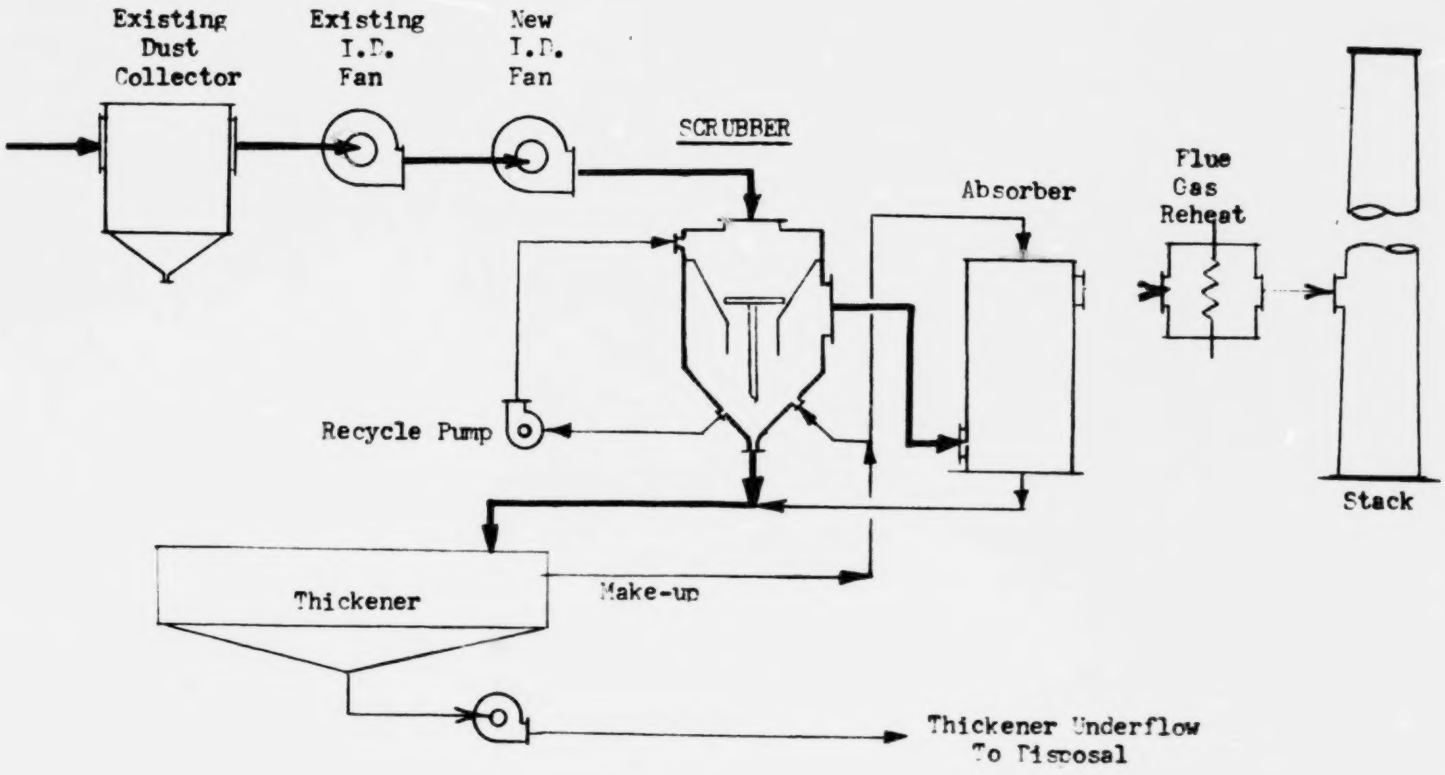
5. Equipment Layout Thus far, the experience of industry with wet type removal systems has demonstrated many problems and poor reliability. Consequently, careful attention must be given to the layout and arrangement of the system. Ready access must be provided for maintenance, repair, and replacement of equipment.

6. Guarantees On the subject of guarantees, a manufacturer may be able to design equipment to meet given proformance specifications and meet a certain particular guarantee. However, I do not believe you will find a manufacturer who will guarantee the performance of his equipment over the period of its useful life. This is, in effect, what the regulatory agencies require of the utility operator.



ARIZONA PUBLIC SERVICE COMPANY
FOUR CORNERS PLANT-SCRUBBER INSTALLATION
SIMPLIFIED FLOW DIAGRAM

W.H.E.
10-20-71



ARIZONA PUBLIC SERVICE COMPANY
CHOLLA POWER PLANT-SCRUBBER INSTALLATION
SIMPLIFIED FLOW DIAGRAM

W.H.E.
10-20-71

DETROIT EDISON FULL-SCALE DEVELOPMENT PROGRAM FOR ALKALI SCRUBBING SYSTEMS

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Detroit Edison Company
Detroit, Michigan

Prepared for
Second International Lime/Limestone
Wet Scrubbing Symposium
New Orleans, Louisiana
November 8-12, 1971

The text material for this paper was included in Paper No. 4c, "Detroit Edison Pilot Plant and Full-Scale Development Program for Alkali Scrubbing Systems--A Progress Report." Therefore the paper is not presented here. J.H. McCarthy and J.J. Roosen of Detroit Edison Company were the co-authors of both presentations.

A FULL SCALE LIMESTONE WET SCRUBBING SYSTEM FOR THE UTILITY BOARD OF THE CITY OF KEY WEST, FLORIDA

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In early 1972, the Utility Board of the City of Key West will put into operation a full scale limestone wet scrubbing system on the initial 37 MW unit of its new power plant, now under construction.

This presentation outlines the decisions which led to the installation of the system and includes a description of the system, economics, proposed operation, and possible operating problems.

INTRODUCTION

Key West, an island city, is approximately five square miles in area and located 160 miles southwest of Miami, Florida. Key West, as well as the entire State of Florida, is widely known for its tourism, fishing and water recreation, and is boastful of its clean and clear water.

The Utility Board of the City of Key West provides electrical energy for Key West, the U. S. Navy, and adjacent communities in the lower keys. The generating facilities for the system are currently comprised of approximately 60 MW of steam power plant generating equipment and 17 MW of package diesel generators.

In early 1968, design was started on a 37 MW power plant to be located on Stock Island, adjacent to the City of Key West. The plant was required to maintain firm capability to meet the growing system load.

In recognition of the increasing emphasis on the protection of the environment and pollution control by both private citizens and governmental agencies at all levels, the Utility Board established a policy of considering all practical methods of controlling pollution at the new power plant.

At the time the plant design was being completed, the air pollution control requirements for the State of Florida were under revision. Consultation with the Florida State Director of Air Pollution and the Southeastern Regional Director of Air Pollution for the Federal Government revealed that the revised criteria would be relatively strict with regard to SO_2 and particulate flue gas emissions.

The fuel for the new plant was residual oil, selected on the basis of availability and economics. The residual oil available at the time contained approximately 2.75% sulfur. The fuel oil suppliers advised that residual oil would be available at some time in the future with a sulfur content of about 0.8%. However, even with the lower sulfur content, preliminary calculations indicated that the future air pollution control requirements could not be met without some form of pollution control equipment.

The Board's policy to control pollution, coupled with the certain adoption of new air pollution restrictions and public opinion, resulted in the inclusion of an SO_2 and particulate scrubbing system as a part of the steam generator specifications. The scrubbing system was included as an alternate bid item to allow the scrubbing systems to be evaluated separately.

A number of scrubbing processes were at various stages of development at the time, but there was some doubt as to their commercial success. However, there appeared to be sufficient prospective economies in using a scrubbing system to warrant careful investigation.

DESIGN PARAMETERS

Once it was established that some form of flue gas scrubbing should be considered, a survey of candidate processes was made.

Some of the factors considered were:

1. Estimated capital costs.
2 Estimated operating costs.
3. State of development.
4. Simplicity of Process.
5. Availability of raw materials.
6. Operating flexibility.

Based on the evaluation of these factors, the limestone wet scrubbing system was selected for primary consideration.

The scrubbing systems normally employ scrubbing devices with proprietary designs. For this reason the specifications were developed on a functional or performance basis, with the primary purpose to obtain proposals on equipment which would be suitable for continuous operation with a base loaded power plant.

Some of the functional requirements included were:

1. A guarantee of SO_2 and particulate removal as follows:
    a. 85% of SO_2 produced when burning fuel oil with a 2.75% sulfur content.
    b. 95% of all particulate matter generated during the combustion process.
2. The scrubbing liquid was to be a slurry consisting of sea water and native coral marl. The marl (limestone) is the primary constituent of all land areas in the Keys, and is consequently readily available. Sea water rather than fresh water was specified due to the extremely high cost of fresh water in the area (in excess of $2.00/1000 gallons.)
3. A complete system was required, including tanks, conveyors, pulverizers, storage bins, pumps, piping and controls. The raw marl delivered to the system was specified to be a maximum size of 2 inches in diameter.
4. Materials of construction were required that would withstand the corrosive effects of a sea water and marl slurry in contack with flue gas. It was further required that the scrubber be designed to safely withstand a gas temperature of 650° F in the event of an air preheater failure.
5. It was required that the spent slurry be of such quality that the sea water could be discharged into the bay and meet all applicable pollution restrictions once the solids had been precipitated out in a settling pond.
6. The manufacturers were required to submit operating costs for the system to be used in evaluating the proposals.

The specifics of design necessary to meet these requirements were established as the responsibility of the manufacturer submitting the proposal.

EVALUATION OF PROPOSALS

Four proposals were received for steam generating equipment, three of which included proposals for limestone wet scrubbing equipment.

Values listed in the proposals for the scrubbing equipment ranged from $345,000 to $738,000. Although it appeared that there was some economic justification in installing a wet scrubbing system, a bid analysis was completed which indicated that the lowest bid for the steam generator and wet scrubbing system was substantially in excess of the funds available. For this reason, the steam generator contract was awarded without the wet scrubbing system.

At this time it was learned that the National Air Pollution Control Administration was in a position to make certain funds available for a full scale limestone wet scrubbing system.

A request was made by the Utility Board of NAPCA that Key West be considered for the installation of a limestone wet scrubbing system, to be jointly funded by the Utility Board and NAPCA. A series of negotiations took place which resulted in a jointly funded full scale limestone wet scrubbing system for the power plant. The system selected for the project was designed by Zurn Air Systems. The Zurn system was selected on the basis of the lowest total evaluated bid which complied in principle with the specifications. The scrubbing device is described by the manufacturer as a modified impingement type scrubber.

Concurrently with the negotiations between the Board and NAPCA, a series of pilot plant tests were conducted at the existing Key West Power Plant using the Zurn Air System's scrubbing device, which demonstrated the feasibility of the system.

A flow diagram for the complete scrubbing system and a schematic diagram of the scrubbing device are shown on Exhibit I.

DESIGN AND CONSTRUCTION

A change order to the steam generator contract was executed in October, 1970, to include the wet scrubbing system. Design and construction progressed at a rapid rate and at the present time the installation is approximately 70% complete.

A considerable amount of review during the design phase was exercised by the Utility Board and their Consulting Engineers as well as by the Office of Air Programs for the Environmental Protection Agency (previously designated as NAPCA) to provide as much constructive input into the design as possible.

Design areas of particular interest were as follows:

1. Material selection -
   The ability of the materials used to withstand the corrosive conditions was considered critical to the successful operation of the system. Although it was known that it might be necessary to replace certain parts of the system with more "exotic" materials during the initial operating period, materials were selected which appeared to be the most practical from economic as well as performance aspects. In general, stainless steel combined with non-metallic coatings was used whenever corrosive conditions were anticipated. Some material selections were based on experience gained during the pilot plant tests.
2. Safety -
   The performance of the wet scrubbing device is directly related to the slurry level in the scrubbing device. Close control of the slurry level is required. Interlocks, automatic overflow devices, and an automatic flue gas bypass were included in the design to avoid the possibility of the slurry level rising above the tubes and consequently blocking off the flue gas flow. Additional interlocks and safety devices were included to protect materials not designed to withstand the high inlet gas temperatures in the event of sea water supply failure.

3. Operation -
   The control system was designed to allow normal continuous operation of the scrubbing system under a relatively constant load. Automatic operation and simplicity were considered to be key design criteria for the controls. Provisions for instrumentation required during the Office of Air Programs' test were included.

Additional design criteria were established by the manufacturer as a result of the pilot plant tests being conducted in Key West.

The general arrangement of equipment for the system is shown on Exhibits 2 and 3.

The entire power plant, including the scrubbing system, is scheduled for start-up in the early part of 1972.

PROPOSED OPERATION

No operating experience other than that gained during the operation of the pilot plants is available since the wet scrubbing system for Key West is still under construction. Therefore, the procedures outlined in this section are tentative, and will be modified as required when the system is put into operation.

The various components of the wet scrubbing system and the material flows are shown on the flow diagram, Exhibit I.

In general, the wet scrubbing system is divided into two sections: The first section is the marl preparation plant. Here coral marl, 2 inches in diameter or less, is received in a pick-up hopper, and after initial crushing to 3/4 inch size is placed in the storage bin. The bin has sufficient capacity to hold a 2-day supply of marl under full load conditions. The material handling equipment up to this point is operated from local manual control stations, on an intermittent basis.

The marl is then fed through a roller mill which reduces the particle size to 90% - 325 mesh, and then on to the surge bin, ready for mixing with sea water. The roller mill feed rate is not easily adjustable and for this reason must be set for the average expected load condition. It must be started manually and will run continuously.

The second section of the system is the actual scrubbing section. Here marl is fed in correct proportion to sea water from the surge bin into the mixing tank to form the desired slurry concentration.

The slurry is pumped to the two scrubbers, each handling half the flue gas. The partially spent slurry is pumped out of the scrubber, some being recirculated to the scrubber and the remainder being pumped to the settling ponds. The slurry flow to the scrubbers and the slurry level in the scrubbers are automatically controlled, based on manual set points established in the main power plant control room. The set points are determined by the unit load and readings from the SO_2 monitor located in the stack.

The flue gas passes from the induced draft fan through a spray section where the gas is cooled from 350° F to 160° F. It then passes through the scrubbers where the SO_2 and particulates are removed, and then to the stack. The flue gas pressure drop across the scrubber is about 12 inches H_2O and is a function of the slurry level in the scrubber.

The scrubbing section can be run on a relatively automatic basis from the main control room once the equipment has been started. A number of automatic controls are included to allow safe operation of the unit. A bypass around the scrubbers is provided for maintenance purposes.

The Office of Air Programs of the Environmental Protection Agency will be performing tests on the system during the first year of operation. It is anticipated that these tests will aid in establishing the optimum flow rates and equipment operation.

Two settling ponds will be provided. One will be emptied while the other is in use. It is anticipated that a front-end loader will be required to handle this material.

POSSIBLE OPERATING PROBLEMS

Anticipated operating problems, particularly in the areas of corrosion, scaling and disposal of spent slurry, are major factors that must be taken into consideration in formulating operating procedures.

The problems of corrosion and scaling were observed in the initial operation of the pilot plants and resulted in material and design changes. It is anticipated that it will be necessary for the contractor to make a number of additional changes once the system is put into operation.

To combat corrosion, the stainless steel scrubbers were epoxy lined and the tube material was changed to fiberglas. It is possible that the change of tube material will also solve the scaling problem, but if not, it was discovered that by installing sprays and maintaining the tubes in a constant wet condition the scaling problem would be eliminated.

Disposal of 50 tons per day of spent slurry is an obvious operating problem and has not been completely resolved to date. The initial thinking was that of utilizing the product to fill approximately twenty acres of City owned baybottom land adjacent to the steam plant site. Although this matter is still being pursued, the State of Florida's recent stand of opposing the filling of any submerged land productive to marine life has made it a less plausible solution.

Initially the slurry will be placed on land above sea level to avoid this problem. Other methods of disposal are currently being investigated.

Wind tunnel tests were conducted during the design of the system to determine if a reheat system would be required for the flue gas. The results were inconclusive. It will therefore be determined during the initial operation of the plant if this will be a problem.

SYSTEM ECONOMICS

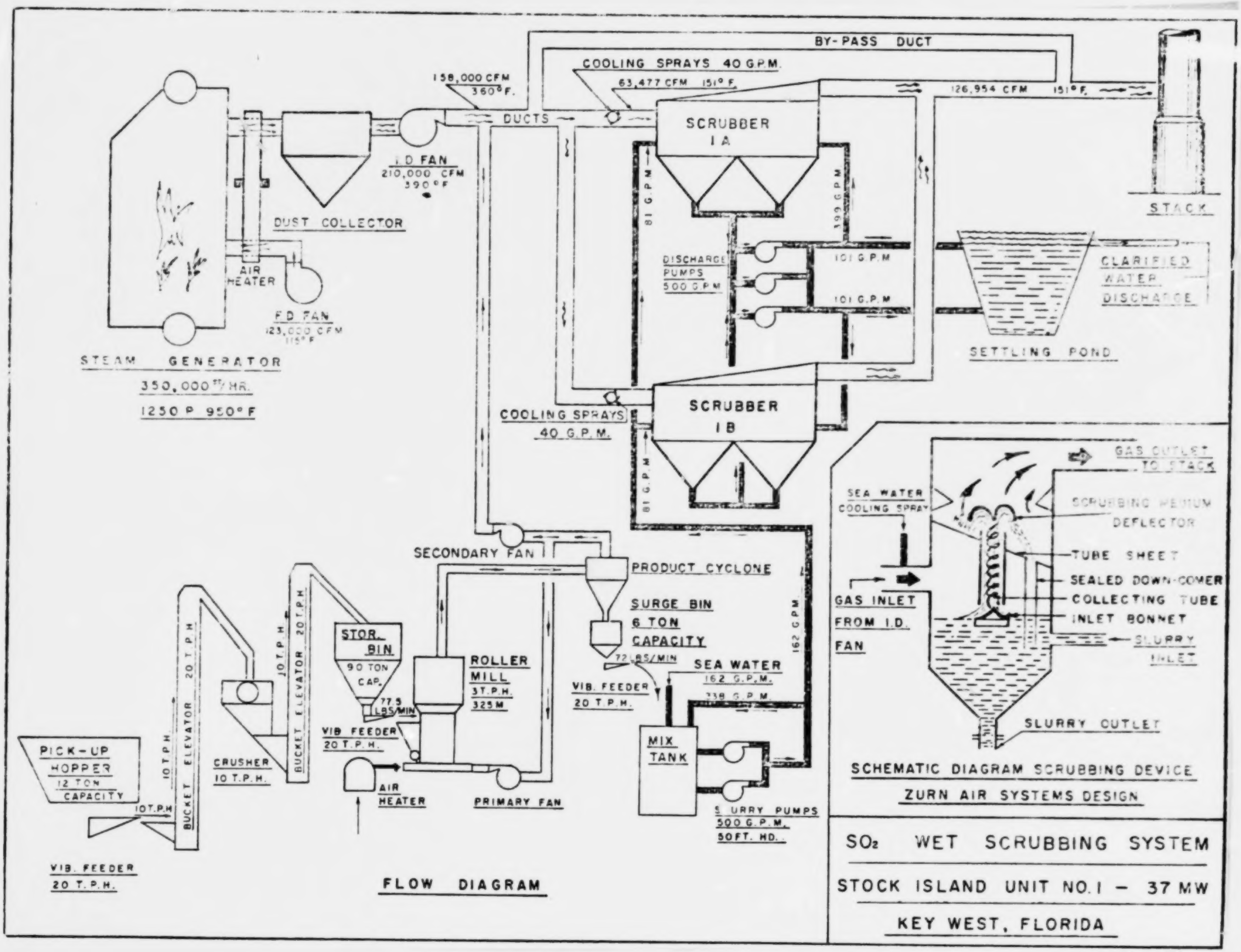
The cost information shown on Exhibit IV summarizes the estimated capital investment requirements and operating costs for the scrubbing system. A cost evaluation, also shown on this plate, relates the system costs to the plant capability and output, and also compares them to the cost of burning low sulfur fuel.

CONCLUSIONS

The mandate has been issued to limit SO_2 and particulate emissions from power plants.

The limestone wet scrubbing process does not appear to be the universal answer in reducing these emissions, but is considered to be the best economical selection for the Stock Island Plant. It is likely that the selection of limestone wet scrubbing equipment will become economically more attractive as the demand for low sulfur fuel increases.

A certain number of operating problems must be expected during the initial phases of operation, but it is anticipated that the solutions to these problems are available within the limits of the current technology.



SCHEMATIC DIAGRAM SCRUBBING DEVICE

ZURN AIR SYSTEMS DESIGN

FLOW DIAGRAM

SO₂ WET SCRUBBING SYSTEM

STOCK ISLAND UNIT NO. 1 – 37 MW

KEY WEST, FLORIDA

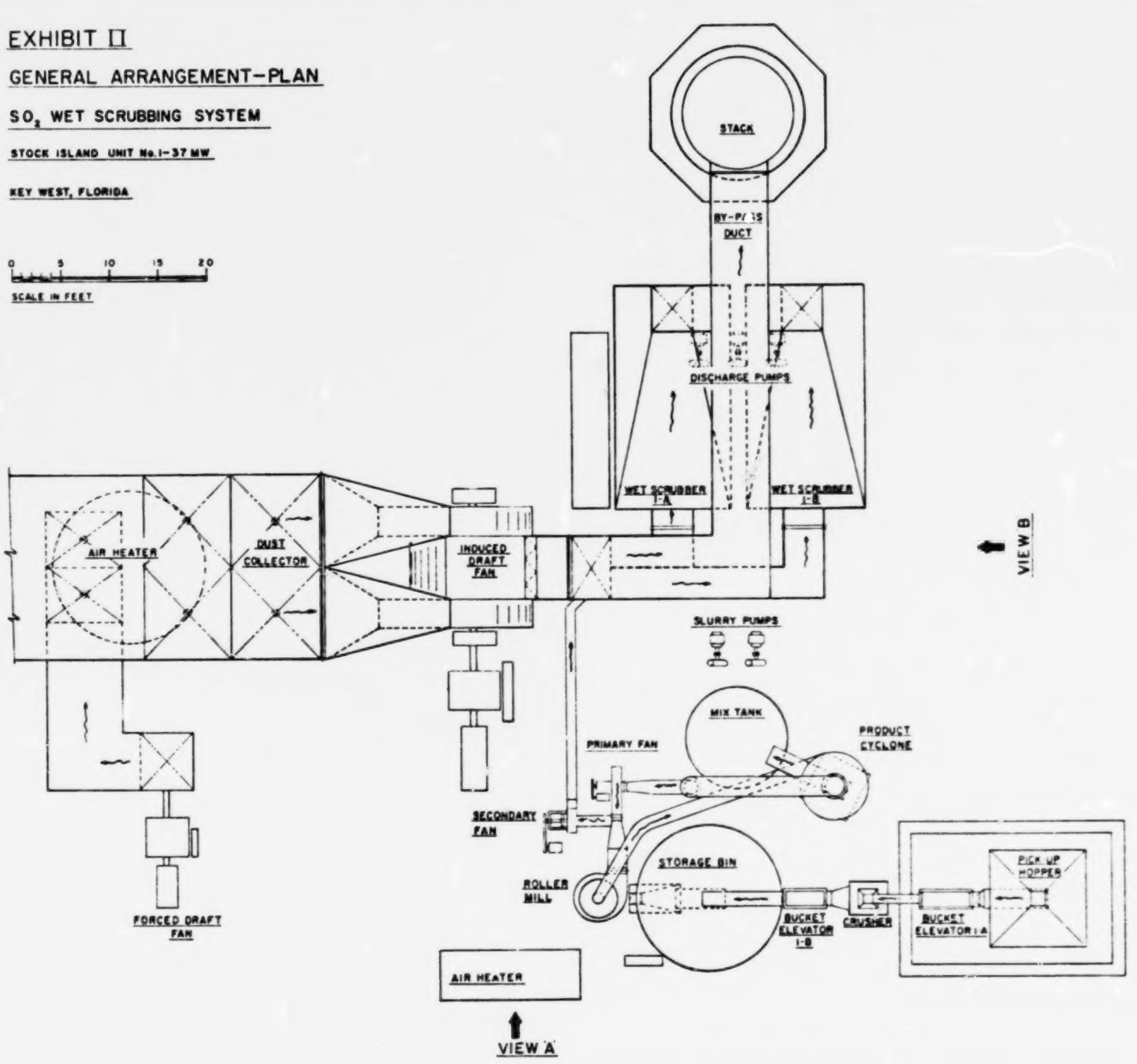
EXHIBIT II

GENERAL ARRANGEMENT-PLAN

SO_2 WET SCRUBBING SYSTEM

STOCK ISLAND UNIT No. 1-37 MW

KEY WEST, FLORIDA



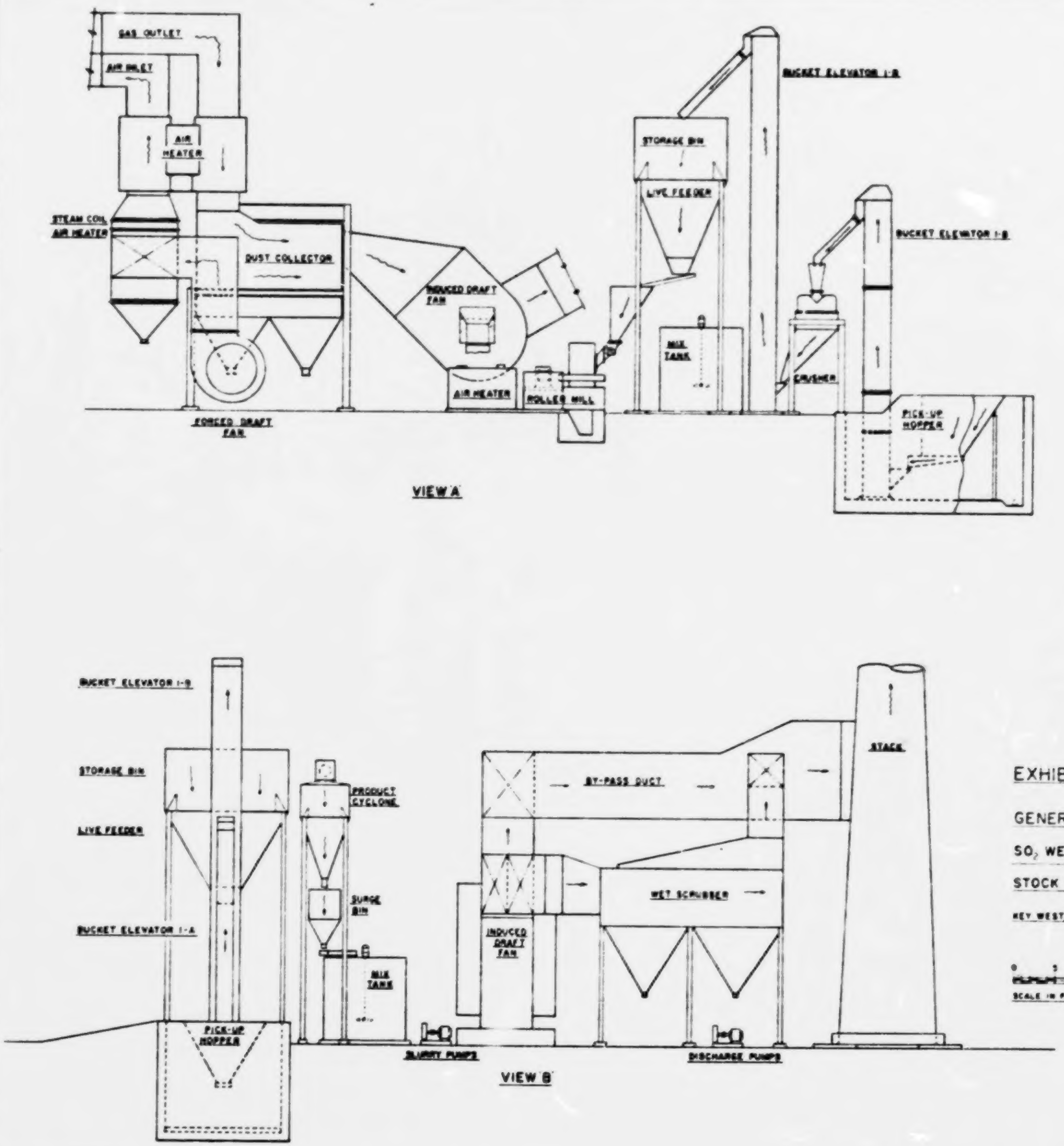


EXHIBIT III

GENERAL ARRANGEMENT-ELEVATIONS

SO_2 WET SCRUBBING SYSTEM

STOCK ISLAND UNIT No I-37MW

KEY WEST, FLORIDA

EXHIBIT IV
SYSTEM ECONOMICS
SO_2 WET SCRUBBING SYSTEM
STOCK ISLAND UNIT NO. 1 - 37,000 KW
KEY WEST, FLORIDA

A. ASSUMED OPERATING COSTS AND CONDITIONS

1.	Annual unit load factor (1)	85% (31,500 kw)
2.	Steam generator design fuel firing rate (2)	23,200 lbs./hr
3.	Fuel	No. 6 residual oil
4.	Fuel sulfur content (maximum)	2.75%
5.	Marl (limestone) cost	$2.00/ton delivered
6.	Incremental cost of low sulfur fuel (3)	$ .40/BBL
7.	Sea water cost	Neg.
8.	Auxiliary Power cost	9 mills/kwhr
9.	Stoichiometry of scrubbing chemical reaction (2)	1:2

B. CAPITAL INVESTMENT REQUIREMENTS (4)

1.	Marl preparation and scrubbing equipment, tanks, pumps, piping, control equipment	$438,700
2.	Incremental cost of additional I. D. fan capacity, ductwork, structural steel	106,300
3.	General construction, including site preparation, foundations, settling pond	33,700
4.	Electrical construction including motor control centers, conduit wiring	64,400
5.	Mechanical construction including wet scrubbing control panel, piping, pneumatic control tubing	27,300
6.	Material handling equipment for marl and spent slurry	30,000
7.	Engineering	50,000
	TOTAL	$750,400

C. ANNUAL OPERATING COSTS

1.	Marl (limestone)	$32,200
2.	Auxiliary power	
	a. I. D. Fan	22,500
	b. Material handling and wet scrubbing system	13,300
3.	Labor	20,000
4.	Maintenance and repair (5)	22,000
		$110,000

D. COST EVALUATION

1. Capital Cost /Kw Plant Capability

$$\frac{\$750,400}{37,000 \text{ kw}} = \$20.30/\text{kw}$$

2. Total Equivalent Annual Cost

a. Annual operating cost $110,000

b. Equivalent annual cost of capital investment (6) 75,400

TOTAL $185,400/year

3. Bus Bar Operating Cost/Kwhr

$$\frac{\$110,000/\text{year}}{37,000 \text{ kw} \times .85 \times 8760 \text{ hours/year}}$$

$$= 0.4 \text{ mills/kwhr}$$

4. Bus Bar Total Cost/kwhr

$$\frac{\$185,400/\text{year}}{37,000 \text{ kw} \times .85 \times 8760 \text{ hours/year}}$$

$$= 0.67 \text{ mills/kwhr}$$

5. Annual Cost Comparison of Wet Scrubbing System vs. Use of Low Sulfur Fuel

a. Low sulfur fuel oil (7)

23,200 lb/hr x .85 L.F. = 19,700 lb/hr or 58.1 BBL/HR

58.1 BBL/HR x 8760 = 510,000 BBL/YR

510,000 BBL/YR x $0.40/BBL = $208,000

b. Wet scrubbing system (8) 185,400

Net Difference $ 22,600

FOOTNOTES:

(1) Based on fact that newest unit has best heat rate and will be base loaded.

(2) Based on proposal from Erie City Energy Division.

(3) Based on estimate from current fuel oil supplier. Assumed to be for 0.8% sulfur content fuel.

(4) Capital costs based on Contract Prices where available. NAPCA funds not included in analysis.

(5) Estimated at 5% of marl and scrubbing equipment cost.

(6) Estimated at 10% per year of capital investment.

(7) Annual cost does not include cost of equipment to handle low sulfur fuel with a high pour point.

(8) 85% efficiency of scrubber is equivalent to burning fuel oil with sulfur content of less than 0.5%.

AIR POLLUTION CONTROL AT THE NORTHERN STATES POWER COMPANY SHERBURNE COUNTY GENERATING PLANT

By

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Presented Before
The Second International
LIME/LIMESTONE WET-SCRUBBING SYMPOSIUM
New Orleans, Louisiana
1971

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SHERBURNE COUNTY GENERATING PLANT

UNITS NO.1 AND NO. 2

ACKNOWLEDGEMENTS

The authors express their appreciation for the suggestions by the many people from Northern States Power Company and Black & Veatch who reviewed the paper.

ABSTRACT

The paper describes the Air Pollution Control System and related considerations of the two-unit Sherburne County Generating Plant. The plant will be located near the Mississippi River about 40 miles northwest of Minneapolis and will have a net capacity of 1360 MW. Fuel will be low sulfur western coal delivered by unit train. Commercial operation of the two units is scheduled for 1976 and 1977 respectively.

Northern States Power Company (NSP) encouraged the formation of the Citizens Advisory Task Force comprising concerned citizens and representatives of public agencies and conservation organizations. This group's contribution in the plant site selection and in the development of environmental protection criteria is discussed.

The authors present the background and considerations which led NSP to the decision to use a limestone wet-scrubber for particulate collection and SO_2 removal. The scrubber selected is the Combustion Engineering Tail-End Limestone Additive System using a 10 inch layer of glass marbles as the contactor. The paper describes the components and physical arrangement of equipment as well as simplified flow diagrams and operating features. The status of the scrubber system development including effluent control, cost estimates, and schedule requirements is given.

AIR POLLUTION CONTROL AT THE NORTHERN STATES POWER COMPANY SHERBURNE COUNTY GENERATING PLANT

INTRODUCTION

Northern States Power Company (NSP) will construct a two-unit, 1360 MW electric generating plant near Becker, Minnesota for commercial operation in 1976 and 1977. The fossil fuel plant, named Sherburne County Generating Plant, will burn low sulfur western coal.

The two previous NSP base-load generating plants are nuclear plants, and it was NSP's desire to build a nuclear plant for commercial operation in 1976 and 1977. Due to the regulatory uncertainties at both the State and Federal level, the growing public resistance to siting of nuclear plants, and finally the amount of nuclear generating capacity in the Company's system, a decision was made to proceed with a fossil fuel plant. Through concerted efforts to involve the public in environmental planning, the use of low sulfur coal, and the use of advanced technology for pollution control, it appears that a coal-fired plant will provide acceptable environmental protection and avoid delays associated with nuclear plants.

PLANT DESCRIPTION

The Sherburne County Generating Plant is located in Becker Township, Sherburne County, Minnesota, approximately 40 miles north of Minneapolis. (See FIGURES 1 and 2.) The site area is about 1,300 acres.

The site is now cultivated land with an average elevation of 965 feet above mean sea level. The land is nearly level, with a maximum elevation differential of about 10 feet. The main plant facilities are set back more than half a mile from the Mississippi River, so that an undisturbed zone is maintained along the waterfront. (See FIGURE 3.) The normal river water elevation is 920 feet mean sea level.

The plant will comprise two electric generating units (Units No. 1 and No. 2) each rated at 680,000 kilowatts net electric generating capacity. The steam generators, turbine generators, wet scrubbers, and associated auxiliary equipment will be enclosed in the main building structure. Unit No. 1 is scheduled for commercial operation on May 1, 1976, with Unit No. 2 scheduled for operation one year later.

Black & Veatch (B&V), Kansas City, Missouri, is the Architect-Engineer and has overall design responsibility for the plant. Management of design, construction, and quality assurance is the responsibility of NSP's Plant Engineering and Construction Department.

Capital expenditures are estimated to be over $360,000,000 for the plant. This includes more than $25,500,000 for the air pollution control system.

The steam generators will be supplied by Combustion Engineering, Inc., and will be of the balanced-draft type designed for burning pulverized coal. Each steam generator will be rated at 4,985,000 pounds of steam per hour and will require a gross heat input of 6,757 million Btu per hour.

Each turbine generator will have a gross capacity of 720,000 kilowatts and will be supplied by General Electric Company. The turbine inlet steam pressure will be a nominal 2,400 pounds per square inch (psig). The inlet steam temperature will be 1,000 degrees Fahrenheit (F) and the reheat temperature will be 1,000 F. Each generator will have a rating of 800,000 kVA at 0.90 power factor.

The furnace will be equipped with tilting tangential burners and will be designed for low combustion temperatures which are expected to reduce to the practical minimum the formation of nitrogen oxides.

Each steam generator will be equipped with a wet flue-gas scrubber, capable of removing 99 per cent of the particulate matter and 50 per cent of the sulfur dioxide in the combustion gases. The scrubbers are described in greater detail later in the paper.

Combustion gases leaving the scrubbers of the two units will be emitted to the atmosphere from a single chimney at least 550 feet tall.

Each electric generator will be connected through a power transformer to a transmission substation. The substation will feed four 345 kV transmission lines supplying power to the existing NSP electrical transmission system.

The turbine condensers will be cooled with water from cooling towers operated as part of a closed-cycle circulating water system. The towers will be of the wet, mechanical-draft, cross-flow type and will be oversized to minimize visible plumes. The cooling tower for each unit will consist of 20 cells, each equipped with a 28-foot diameter fan capable of moving about 1,500,000 cubic feet of air per minute. The air-vapor mixture will be discharged from individual fan stacks about 60 feet above grade. The circulating water flow rate for each unit will be approximately 240,000 gallons per minute (gpm). The cooling tower for Unit No. 1 will be located 3,000 feet from a similar tower for Unit No. 2 to reduce the combination of plumes from the two towers.

Fuel for the plant will be low sulfur (0.8 per cent or less) subbituminous coal from the Colstrip area of Montana. Coal shipment is to be made by unit trains. Coal handling facilities at the plant site will include automatic sampling facilities, rotary car dumper, stacker-reclaimer, crushing facilities, and a system of conveyors for transfer of coal between elements of the system. A generally circular railroad track, which will handle the unit trains, will enclose the coal storage area at the plant site. Storage at the plant site will provide a 90 day supply of coal. This will require approximately 1,600,000 tons of coal, stored to a depth of about 40 feet. The maximum design burning rate is 814 tons per hour for the two units.

Ash from coal combustion will be collected in the bottom ash hoppers and scrubbers associated with each unit. Ash from these collection points will be sluiced to a water-filled ash storage basin formed by an earthen dike. The bottom of the storage basin will be sealed to minimize seepage into ground water.

Water sources for operation of the plant will be the Mississippi River and wells. After maximum reuse, all process return water from the various plant systems will be directed to a common water holding basin with a minimum retention time of 24 hours. Water for the ash handling systems will be reused process water. All process return water which cannot be recycled will be treated to meet applicable water quality standards prior to release to the river at a single point of discharge.

BACKGROUND OF ENVIRONMENTAL CONTROL

In Minnesota, as in most other states, there has been no effective method of resolving conflicting viewpoints concerning the environmental aspects of power plant siting and development. In an effort to find a new approach to resolution of conflict, NSP discovered that many environmental conflicts involved in its past construction programs arose from a lack of early public participation in its environmental planning activities. Northern States Power Company also realized that the public hearing process is an inadequate method for communicating with the public or involving the public in planning and decision making processes. As a result of evaluating past environmental planning programs, NSP created the Citizens Advisory Task Force to provide a forum for in-depth discussions on environmental problem solving and power plant siting.

Participating in the new open-planning group were representatives from the Minnesota Conservation Federation, the Scientific Study Areas Committee of the Minnesota Academy of Science, Minnesota-Wisconsin Boundary Area Commission, Minnesota Chapter of the Sierra Club, Minnesota Committee for Environmental Information, Minnesota Environmental Control Citizens Association, Minnesota Chapter of the Isaac Walton League, Minnesota Environmental Defense Council, Save Lake Superior Association, Zero Population Growth, St. Croix River Association, Clear Air – Clear Water Unlimited, and the League of Women Voters.

Northern States Power Company believes that it is important to seek out those individuals who can effectively represent the concerned public to assist in major decisions relating to power plant siting and pollution control. There are two reasons for this approach: (1) the installation will more closely represent the public interest; that is, it will be consistent with what the public appears to be willing to pay for, and (2) delays in securing permits and licenses may be avoided by using the advice of those who represent the public.

After about six weekly meetings, the Citizens Advisory Task Force generally lost its hostility toward NSP and developed a deep concern in accomplishing the objective of plant site selection. The group took under advisement four alternate sites to determine which site should be selected for a 680 MW fossil fired power plant to be in service in 1976. The Task Force recommended the Sherburne County site and NSP concurred, even though another location was the Company's first choice.

Northern States Power Company conducted a thorough investigation of alternate methods of air pollution control for Sherburne County, in line with the following Task Force guideline contained in the group's report:

> *Emission of all air-pollutants should be reduced to the minimum technologically feasible. The cleanup should include not only*

> *particulate matter but also gaseous pollutants such as sulfur oxides. The Task Force noted the Company's stated intention to use low sulfur western coal in its next plant, but cautions the Company against regarding this use as removing the need for sulfur oxide cleanup as it becomes technologically feasible for other coals. Adequate space should be provided for future additions of air pollution control equipment to accommodate possible future technological developments and revised air emission standards.*

The collection of fly ash from low sulfur coal is difficult with a "cold" electrostatic precipitator (with a flue gas temperature at the precipitator inlet of about 300 F) due to the high resistivity of the ash at normal exit gas temperatures. There are also problems of energizing a "cold" precipitator at low loads and startup. For these reasons, a "cold" precipitator was not considered practical. The alternatives considered were a "hot" precipitator (with a flue gas temperature at the precipitator inlet of about 700 F) or a wet flue gas scrubber. Even though economics were somewhat in favor of a "hot" precipitator, NSP selected the wet scrubber because there is a high degree of confidence in collecting particulates and there would be some reduction in the sulfur dioxide emissions.

SCRUBBER DESCRIPTION

The air pollution control system includes a tail-end limestone wet scrubber designed to remove both particulate and SO_2 from the boiler flue gases. The manufacturer guarantees that the system will remove 99 per cent of the particulates and 50 per cent of the SO_2 entering the scrubber if either high calcium limestone or dolomitic limestone is used as an additive.

The flue gas enters each module below a bed of glass marbles at a design temperature of 290 F. (See FIGURE 4.) As the gas turns upward, large particles are separated immediately. Sprays provide a constant supply of water to the underside of the bed of marbles. Water entrained in the gas stream floods the spaces between the marbles. Violent mixing and physical contact occurs which results in the capture of substantially all of the particles larger than 5 microns and a high proportion of the particles smaller than 5 microns. The cleaned and cooled moisture laden gas goes up through demisters which remove entrained water. The gases are then reheated from 120 F to about 163 F to (1) provide dry gas for protection of the ID fans, (2) reduce visual pluming at the stack exit and (3) enhance buoyancy which increases the effective stack height. The water containing the particulates overflows the turbulent bed and is drained to a clarifier for particulate concentration.

The SO_2 is removed from the flue gas by chemical reaction with the limestone additive in the marble bed contactor. The overall reaction can be shown as:

$$CaCO_3 + H_2O + SO_2 \longrightarrow CaSO_3 + CO_2 + H_2O$$

and continuing

$$2CaSO_3 + O_2 \longrightarrow 2CaSO_4$$

The calcium sulfate and calcium sulfite are only slightly soluble in water and are therefore mostly precipitated. The precipitated solids are carried with the scrubber bed drain water along with the fly ash to the clarifier for concentration prior to disposal in the ash storage area. The recirculating tank is the source of the scrubber spray water and is made up of the following:

- Clarifier overflow
- Additive slurry
- Makeup water to replace evaporation and blowdown

A soot blower is located in the gas inlet duct to each module to clean the scrubber at the dry gas – moist gas interface. Soot blowers also clean the heat transfer surface of the reheater. Water washers are provided to clean the demister section. Experience gained from operation of the scrubbers at Unit 4 of the Lawrence Station on The Kansas Power and Light Company system indicates that this cleaning equipment will be adequate.

Velocity of the gases through the bed of marbles must be maintained at above 75 per cent of rated flow to create the required turbulence for particulate removal. This is accomplished by automatically removing scrubber modules from service in groups of three as the load is reduced.

The modules are arranged in four groups of three as shown on FIGURE 5, Plan View. Flue gas crossover ducts at the air heater outlet and ID fan inlet permit flexibility of ID fan and module operation. The arrangement will enhance the reliability of operation of the flue gas scrubber system.

The additive will be wet ground and sluiced to the recirculation tank. The feed quantity will be controlled as a function of the amount of SO_2 in the inlet to the scrubber. It is expected that 100 per cent of the stoichiometric ratio will be required for 50 per cent SO_2 removal. Dolomitic limestone (40 per cent $MgCO_3$ – 50 per cent $CaCO_3$) is being considered as an additive because it is available near the plant. High calcium limestone would have to be shipped from areas remote from the plant. The $MgCO_3$ will react with SO_2 to form $MgSO_3$ and $MgSO_4$. The solubility of $MgSO_4$ is very high, which may complicate the ability of the scrubber to form a solid precipitate of the SO_4 ion. This could result in a less desirable blowdown from the scrubber for eventual discharge to the environment.

RESEARCH AND DEVELOPMENT

The scrubber components are well along in the development stage. The scrubber **system** development, however, is still in progress, with emphasis on the following items:

- Reducing quantity of the scrubber system effluent
- Determining quality of the effluent and the effect on river water quality
- Selecting type and determining amount of the additive
- Confirming system and component reliability
- Confirming scrubber performance with respect to the guarantee

A task force comprising personnel from NSP, B&V, and Radian Corporation is working closely with Combustion Engineering to solve these problems.

The highest priority is placed on minimizing the impact of the effluent with respect to both quantity and quality. Tests are being conducted on the Combustion Engineering pilot system in Windsor, Connecticut, to minimize the blowdown from the scrubber system by using a seeded crystallizer tank to precipitate calcium sulfate and calcium sulfite. The tests are being run initially with a high calcium limestone additive. Further tests are planned with dolomitic limestone and western coal fly ash. Radian Corporation is supplying input with respect to reviewing bench studies and analyzing pilot system scrubber chemistry. The design of the scrubber components and scrubber system is under careful review to maximize reliability and performance.

TABLE I and TABLE II summarize the important river water quality parameters that can be affected by the scrubber effluent. The total dissolved solids would be slightly increased immediately downstream of the plant, but this effect would be hardly noticeable at the Minneapolis water intake approximately 35 miles downstream.

TABLE I

RIVER WATER ANALYSIS AT SHERBURNE COUNTY GENERATING PLANT

	Prior to Plant Operation	After Plant Goes Into Operation	
River Flow, cfs		1,223*	3,322**
Dissolved Solids, mg/l			
Ca	40.1	43.6	41.4
Mg	15.6	18.1	16.5
Na	4.8	4.8	4.8
$M(HCO_3)$	181.0	178.4	180.1
SO_4	10.0	30.2	17.4
Cl	3.6	3.6	3.6
NO_3	1.9	1.9	1.9
SiO_2	5.8	5.8	5.8
Total	262.8	286.4	271.5
Carbonate Hardness	148	146	148
Noncarbonate Hardness	16	37	24

* Flow exceeded 90 per cent of the time

** Flow exceeded 50 per cent of the time

TABLE II

RIVER WATER ANALYSIS AT RIVER INTAKES FOR MINNEAPOLIS AND ST. PAUL

	Prior to Plant Operation	After Plant Goes Into Operation	
River Flow cfs		1,729*	4,781**
Dissolved Solids, mg/l			
Ca	46.9	49.4	47.8
Mg	15.4	17.1	16.0
Na	2.1	2.1	2.1
$M(HCO_3)$	207.4	205.6	206.7
SO_4	10.8	25.1	16.0
Cl	4.0	4.0	4.0
NO_3	0.7	0.7	0.7
SiO_2	8.6	8.6	8.6
Total	295.9	312.6	301.9
Carbonate Hardness	170	168	169
Noncarbonate Hardness	10	25	16

* Flow exceeded 90 per cent of the time
** Flow exceeded 50 per cent of the time

Northern States Power Company is actively involved in air pollution control planning. There are a number of areas that NSP believes require more research and development in the near future. Much effort has been made to develop systems that will provide SO_2 control and particulate removal. These areas will require more attention. NO_x emission is becoming a major concern, and NO_x reduction systems will need to be developed.

The water effluent from scrubbing systems must be minimized or eliminated. If there is an effluent, it must be of acceptable quality. It is not prudent to exchange one problem for another. Much effort has been made with respect to particulate removal and SO_2 removal, but very little concern has been given to the blowdown effluent from scrubbing systems.

The design and development of scrubbing systems must consider reliability of operation since the scrubbing system is an integral part of the power plant. Unless the scrubbing system is reliable, the plant itself cannot be reliable.

REFERENCES

California Institute of Technology, Environmental Quality Laboratory, *People, Power and Pollution: Environmental and Public Interest Aspects of Electric Power Plant Siting*, September 1, 1971. Report No. 1.

Black & Veatch, *Northern States Power Company Environmental Report, Sherburne County Generating Plant*, May 24, 1971.

LIST OF FIGURES

FIGURE 1 PLANT SITE LOCATION MAP

FIGURE 2 PLANT SITE VICINITY MAP

FIGURE 3 PLANT SITE ARRANGEMENT

FIGURE 4 FUNCTIONAL SCHEMATIC FLUE GAS SCRUBBER MODULE

FIGURE 5 PLAN OF FLUE GAS SCRUBBER MODULES

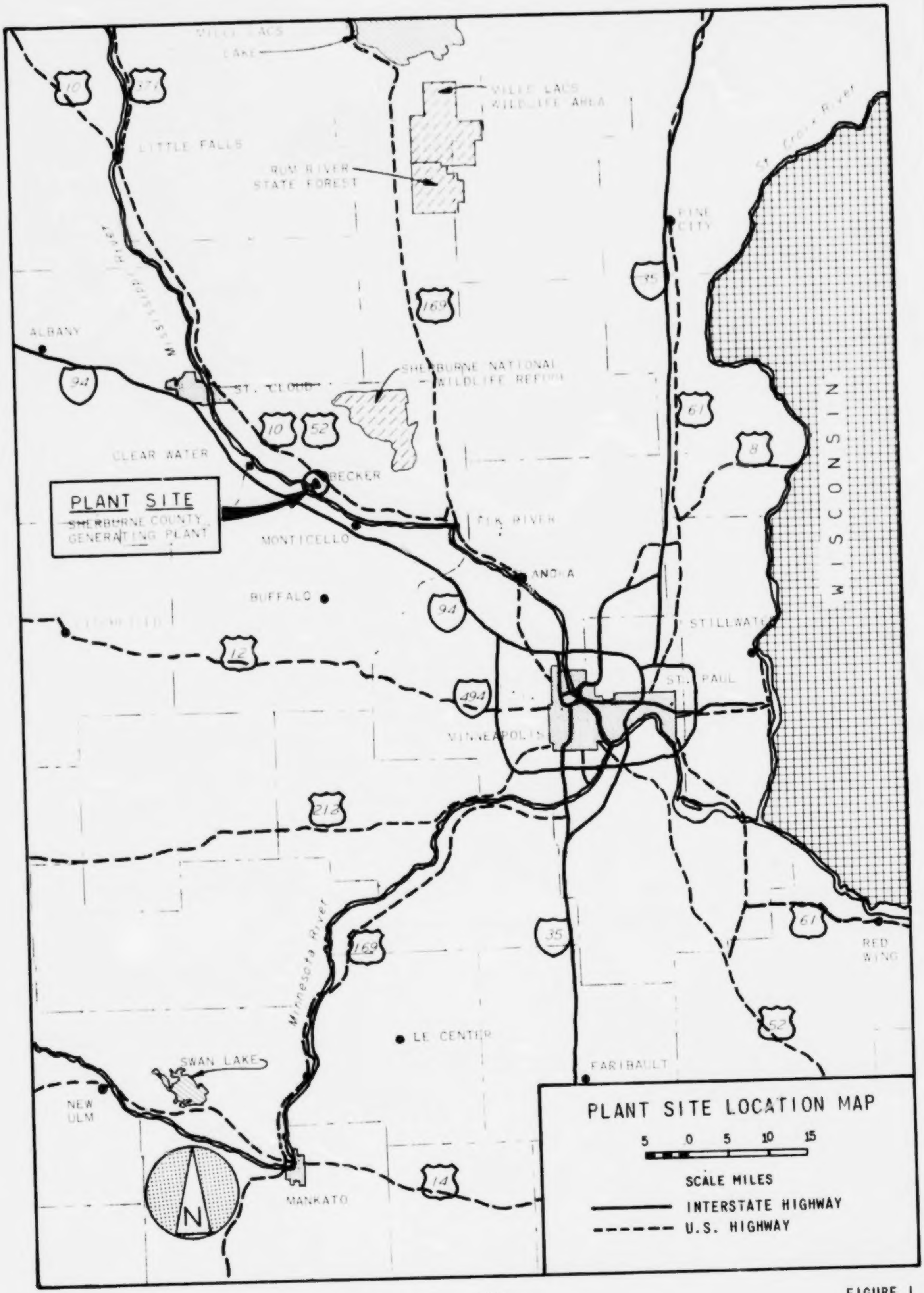

MILLE LACS LAKE
MILLE LACS WILDLIFE AREA
10
371
LITTLE FALLS
RUM RIVER STATE FOREST
St. Croix River
Mississippi River
PINE CITY
35
169
ALBANY
94
SHERBURNE NATIONAL WILDLIFE REFUGE
ST. CLOUD
10
52
61
8
CLEAR WATER
BECKER
PLANT SITE
SHERBURNE COUNTY GENERATING PLANT
MONTICELLO
ELK RIVER
WISCONSIN
ANOKA
BUFFALO
94
LITCHFIELD
STILLWATER
12
ST. PAUL
494
MINNEAPOLIS
212
Minnesota River
61
RED WING
169
35
52
LE CENTER
SWAN LAKE
FARIBAULT
NEW ULM
MANKATO
14
N
PLANT SITE LOCATION MAP
5 0 5 10 15
SCALE MILES
INTERSTATE HIGHWAY
U.S. HIGHWAY

FIGURE I

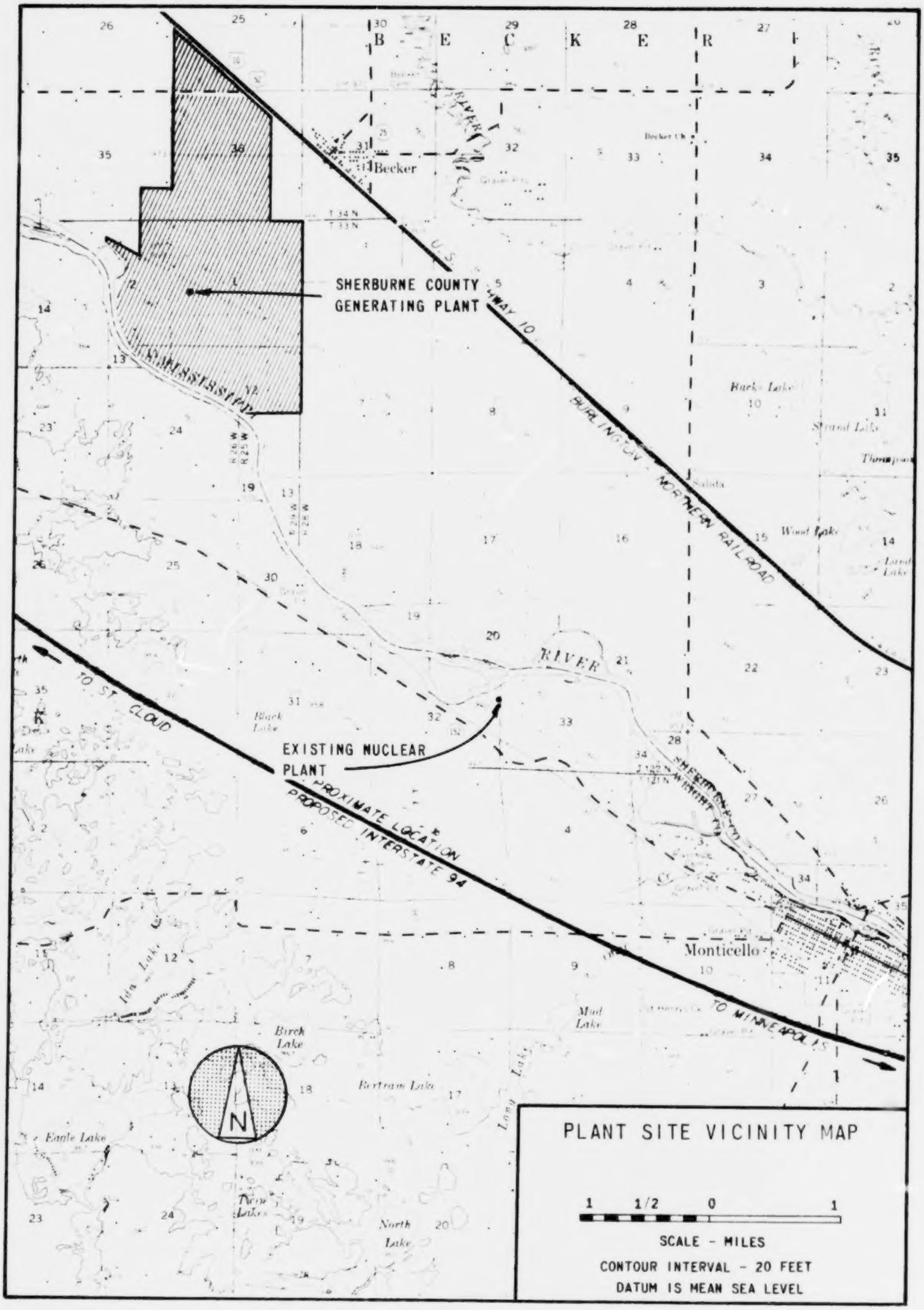
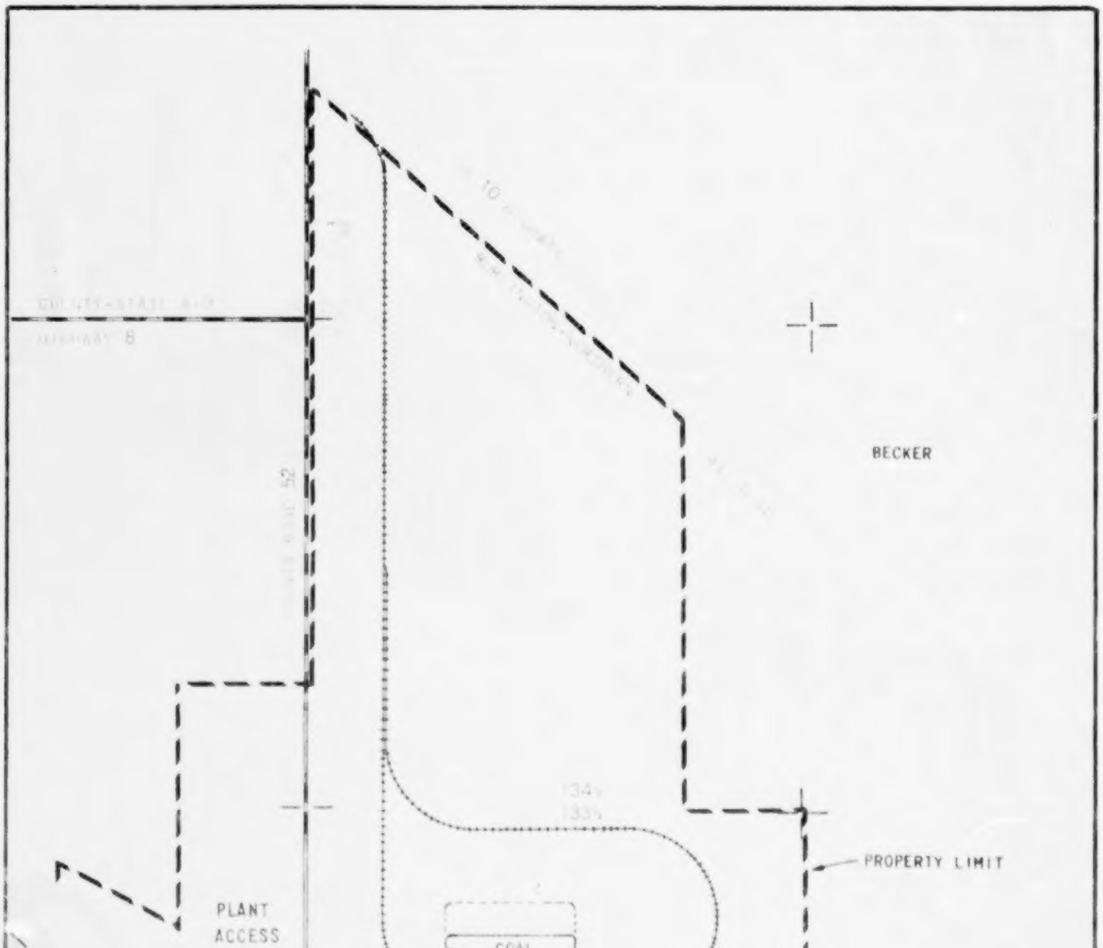
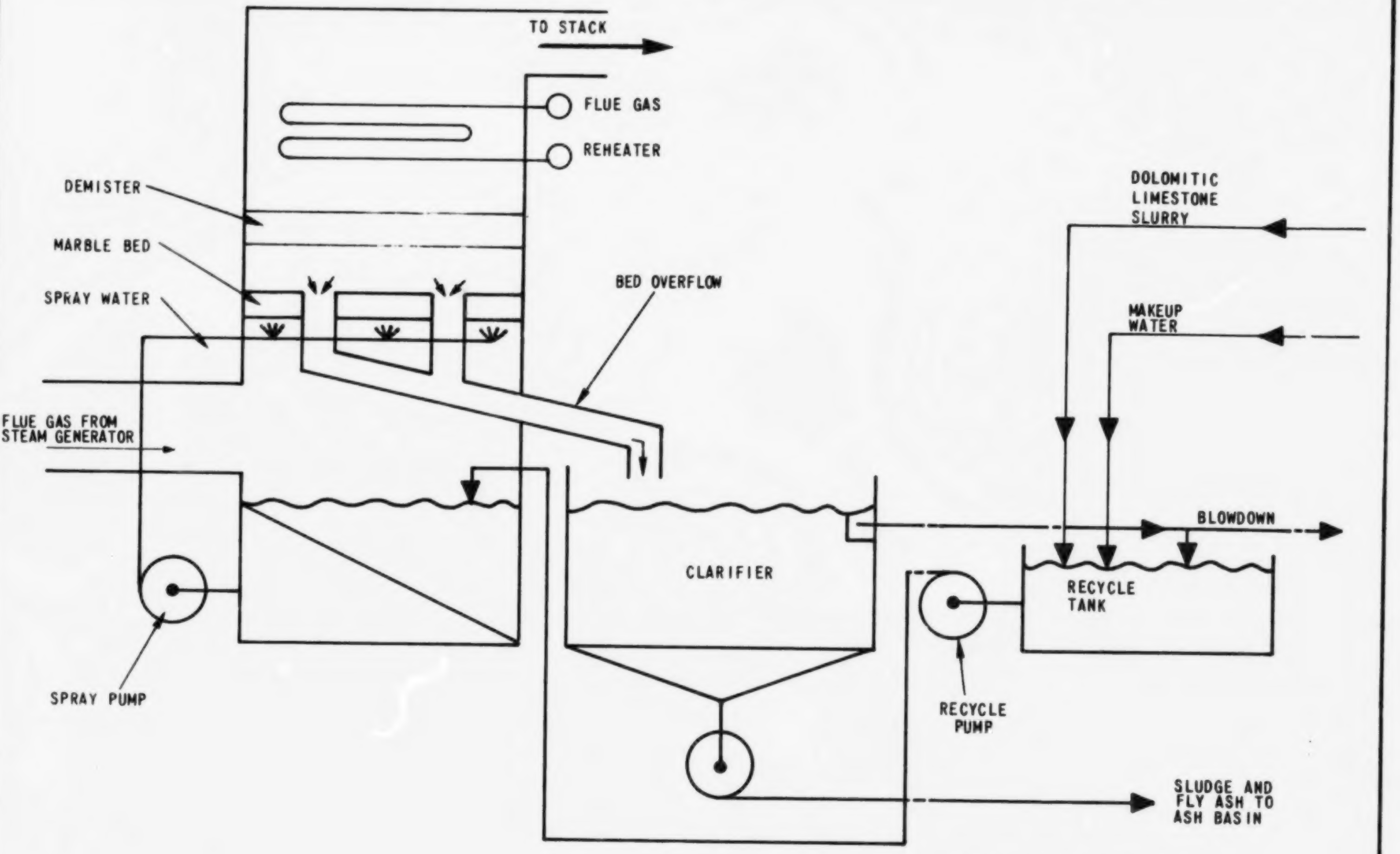

B E C K E R
Becker
U.S. HIGHWAY 10
BURLINGTON NORTHERN RAILROAD
SHERBURNE COUNTY
GENERATING PLANT
MISSISSIPPI
RIVER
T 34 N
T 33 N
Bucks Lake
Wood Lake
Black Lake
EXISTING NUCLEAR
PLANT
TO ST. CLOUD
APPROXIMATE LOCATION
PROPOSED INTERSTATE 94
TO MINNEAPOLIS
Monticello
Mud Lake
Long Lake
Ida Lake
Birch Lake
Bertram Lake
Eagle Lake
Twin Lakes
North Lake
N
PLANT SITE VICINITY MAP
1 1/2 0 1
SCALE - MILES
CONTOUR INTERVAL - 20 FEET
DATUM IS MEAN SEA LEVEL

FIGURE 2



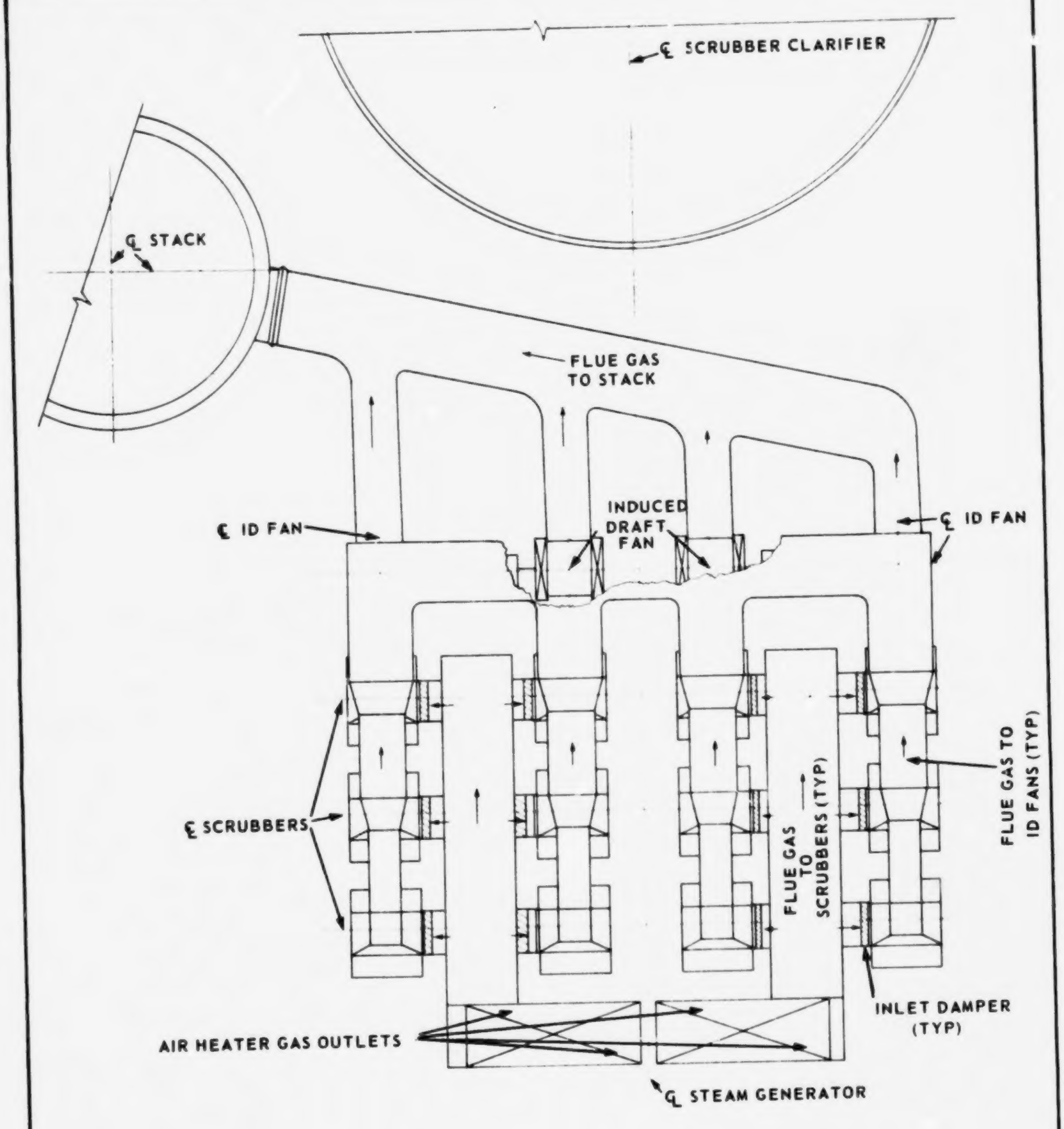
PLANT SITE ARRANGEMENT

FIGURE 3



FUNCTIONAL SCHEMATIC
FLUE GAS SCRUBBER MODULE

FIGURE 4



PLAN OF
FLUE GAS SCRUBBER
MODULES

FIGURE 5

ONTARIO HYDRO'S PROTOTYPE LIMESTONE SCRUBBER FOR SO_2 REMOVAL FROM CLEAN FLUE GAS

J.W. James
Ontario Hydro
Toronto, Canada

Prepared for
Second International Lime/Limestone
Wet Scrubbing Symposium
New Orleans, Louisiana
November 8-12, 1971

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ONTARIO HYDRO'S PROTOTYPE LIMESTONE SCRUBBER FOR SO_2 REMOVAL FROM CLEAN FLUE GAS - by J.W. JAMES

ABSTRACT

Ontario Hydro is currently designing a 30 MW demonstration limestone scrubber and expects to install it at one of its stations near Toronto.

The system, which is planned for initial operation in 1973, will use limestone slurry in a spray tower contactor to scrub SO_2 from clean flue gas. The gas will be cleaned by an existing 99% efficient electrostatic precipitator. This prototype will be sufficiently large to allow confident upscaling to a full size 150 MW module, and should be particularly applicable to existing units fitted with fly ash collectors.

The design of the prototype is based on a system devised by Ontario Hydro's Research Division and tested in a 4000 cfm pilot plant with flue gas from a coal-fired boiler.

The reasoning involved in selection of this system is presented, along with the considerations to be investigated during the tests.

Presented at the Second International Lime/Limestone Wet Scrubbing Symposium, New Orleans, November 11, 1971

ONTARIO HYDRO'S DEMONSTRATION LIMESTONE SCRUBBER FOR REMOVAL OF SO_2 FROM CLEAN FLUE GAS

J. W. JAMES

1. Most of us are now aware that the route to the development of a successful SO_2 removal process leads through a beautiful garden having many inviting and expensive pathways. Choice of the route to follow is influenced by faith, hope, and much scientific endeavour; and is fraught with concern of being led down the wrong garden path. - Having had some exposure to this process, I would like to speak briefly today on the recent choice at Ontario Hydro in favour of a 30 MW scrubber to demonstrate the removal of SO_2 from one of its coal-fired boilers.

2. During the past few years, our top management have been anxious to develop an SO_2 removal process, through work on a large demonstration unit installed in one of our own plants. Many systems have been analyzed with this objective in mind. For a variety of reasons, all were rejected. Some were already being developed in demonstration units, while others were either not suited to our needs or appeared to hold little promise. During this period of search, we entered into two multi-sponsor agreements to support well known major Research and Development projects. However, it was not until the completion of our Research Division's most encouraging work on a 4000 cfm pilot plant, using limestone slurry in a spray tower scrubber, that we had a viable candidate for a large demonstration system for development on one of our generating units.

3. The pilot plant and its performance is described in a paper entitled "Sulphur Dioxide Removal by Limestone Slurry in

a Spray Tower" by A. Saleem, D. Harrison and N. Sekhar. This paper was presented during Tuesday's session. The 4000 cfm pilot plant achieved about 75% removal of SO_2 from clean flue gas which was drawn off the ductwork following the electrostatic precipitator of a 300 MW coal-fired unit. The spray tower operated with a high degree of reliability; and inspection, following a 1000 hour continuous run, indicated no hard scale formation, although some surfaces did have a soft deposit.

4. In general, the large scrubber will be similar to the pilot, and its design will be based on the optimized process variables from the pilot work. Provision will be made to operate at off-design conditions as indicated by the demonstration tests. - Aerodynamic model tests may be necessary to establish the large scrubber vessel shape. These would optimize vessel configuration to accommodate structural and space considerations, while ensuring a satisfactory gas velocity profile in the scrubber and demister over a 25 to 100% gas flow range.

5. The choice of limestone slurry in a spray tower contactor to scrub clean flue gas from 30 MW of generation was based on the following reasoning:

   a) the limestone slurry process appeared to have a better chance of early development than other SO_2 removal processes.

   b) the choice of a spray tower scrubber was based on the pilot plant experience. Some of its advantages are:

      - it holds promise of fairly high reliability. This results from the simplicity of the tower, which has a minimum surface on which deposit can form or collect. Also, deposit formations on the demister and scrubber surfaces are expected to be sufficiently soft to allow removal by slurry or water sprays.

- it is much less sensitive to gas flow turndown than either fixed or moveable bed scrubbers. This is particularly important on our generating system because of the cycling demand on fossil units.
- it has a very low flue gas pressure-drop, and this may allow it to be retrofitted to existing units with minimum modification to the ID fans.
- its SO_2 removal efficiency is expected to be at least 70% and limestone consumption is about 1.3 stochiometric. This is considered to be a satisfactory performance if high reliability is achieved.

c) It was decided to demonstrate SO_2 removal while scrubbing clean flue gas since it reduced the chemical problems introduced by fly ash. All of Ontario Hydro's existing fossil plants are fitted with high efficiency electrostatic precipitators, thus a clean gas system can be directly applied to its existing plants. For new power plants, the environmental pressures for dry disposal of fly ash may result in continued specification of precipitators. Alternatively, substitution of a high efficiency venturi scrubber for particulate removal is not expected to adversely affect the spray tower operation.

d) The 30 MW size was selected to provide the fastest and most economical means of developing a full-scale scrubber. It was assumed that full-scale scrubber modules are unlikely to exceed 150 MW in size during the next few years. Further, it was thought that a successfully operating 30 MW scrubber could be scaled-up to full size with confidence, and applied to a number of operating boilers. Alterations to the 30 MW unit during development will require considerably less time and cost than for a larger scrubber.

6. Areas to be investigated in the demonstration unit are those common to most limestone slurry systems. Some of these are noted below:

a) Scrubber

- The optimized gas velocities and L/G ratios derived in the pilot module are to be verified.
- a major consideration is gas velocity distribution in the scrubber and demister. Attempts will be made to measure and optimize this at critical locations.

b) Demister

Test data are needed in at least three areas:

- The effects of velocity maldistribution and demister cleaning on the amount of solid and liquid particles escaping the demister.
- The optimization of moisture removal versus pressure drop.
- The methods of on-load cleaning.

c) Reheater

Initially the unit will have a direct fired reheater. Upon successful demonstration of the scrubber/demister, other methods of reheating will be tried.

d) Waste Slurry

This will be discharged to a divided settling pond where the slurry is expected to decant to 80% solids. The liquor will be recycled to the process and the solids disposed off-site.

Items requiring investigation include:

- The control of dissolved constituents in the recycled liquor.
- The most economical means of dewatering the slurry on site.

Alternatives to the settling pond include a clarifyer, or a vacuum filter.

- The environmental problems of the solids disposal.

e) Materials

Corrosion rates will be investigated for various materials in contact with the liquid phase.

f) Assessment of process availability and reliability.

7. Regarding design and construction status, preliminary design of the 30 MW unit is in progress and the commitment to final design and construction is scheduled for next March. The unit is expected to be commissioned and ready for testing by September 1973.

8. Ladies and Gentlemen, I am well aware that many plans for the removal of SO_2 have come and gone. However, the plan presented here today is based on considerable recent R&D, and is one in which we have great confidence. I trust that at a future Symposium, we can present demonstrated results of the successful operation of this 30 MW spray tower scrubber.

LA CYGNE STATION AIR QUALITY SYSTEM

by

D. T. McPHEE

KANSAS CITY POWER & LIGHT COMPANY

KANSAS CITY, MISSOURI

presented at

SECOND INTERNATIONAL LIME/LIMESTONE WET SCRUBBER SYMPOSIUM

SHERATON-CHARLES HOTEL

NEW ORLEANS, LOUISIANA

November 8-12, 1971

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LA CYGNE STATION AIR QUALITY SYSTEM

La Cygne steam electric generating station is a 820 mw, 3500 psi cyclone-fired fossil-fuel unit utilizing a local low grade coal and is scheduled for commercial service in 1973. This is a joint venture between Kansas City Power & Light Company of Kansas City, Missouri, and Kansas Gas and Electric Company of Wichita, Kansas. It is estimated to cost between \$180 and \$190 million and each of the companies will have a 50% interest in the plant. Kansas City Power & Light Company is the operating agent and will operate the plant. The fuel will consist of some 2 million tons per year of a low grade bituminous coal obtained from strip mines within a few miles of the plant. Some of the characteristics of this coal are 22% ash, 5-1/4% sulfur, 10,000 Btu per pound. In 1968 when the two companies decided to construct this plant, the decision was made that an adequate air quality system would be installed to fulfill our environmental responsibilities.

This decision has been a bit difficult to carry out in that we have been faced with a moving target in trying to identify our environmental responsibility and as originally anticipated, have had to carry out a crash program to develop a technology for removal of SO_2 as well as particulate matter. I do not want to belabor the moving target part of the problem, but bear in mind that it certainly has been and still is substantial. With a vast amount of emotionalism, and a fair degree of bureaucratic and political nonsense that invariably creeps into important new broad base concerns of man, it has been a bit difficult to accurately and realistically identify the environmental problem.

However, regardless of this and regardless of the fact that a new technology must be hurriedly ushered onto the electrical generating scene, Kansas City Power & Light Company and Kansas Gas and Electric Company keenly feel that the new dimensions of our environmental responsibility requires that we forge ahead with an adequate air quality system for La Cygne.

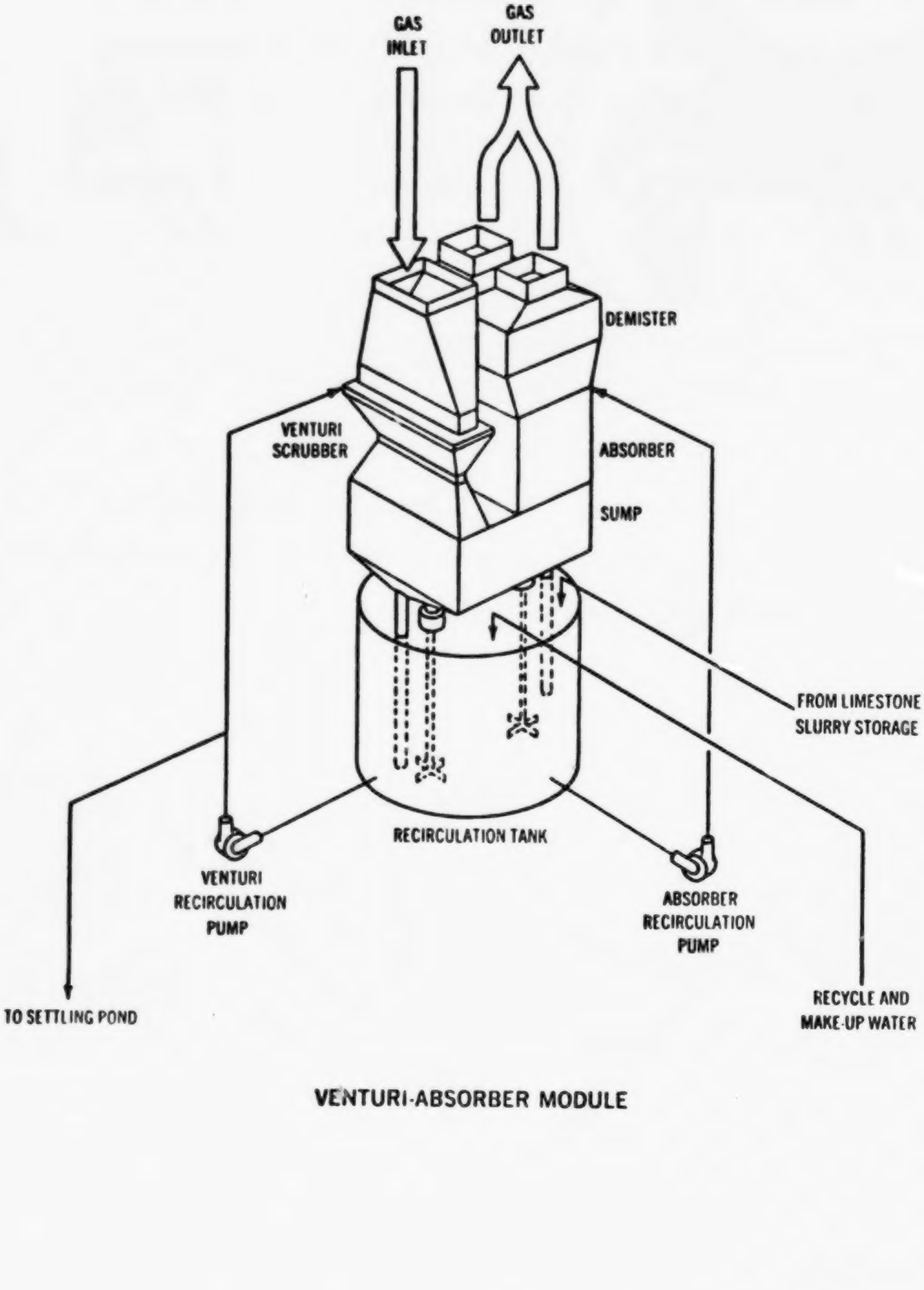
A substantial development program was carried out preparatory to the decision on the type of equipment. Some $300,000, mostly with Ebasco Services, Inc. and Chemical Construction Company, went into this effort over an 18-month period. We also took a look at the sulfur and sulfuric acid market for the metropolitan area of Kansas City. The results of this investigation were not favorable for a recovery type of system. Our review of the status of technology also indicated that some type of lime or limestone non-recovery type of system should be used. Discussions were carried out with Chemical Construction Company, Babcock & Wilcox and Combustion Engineering for providing a system that would remove particulate matter and sulfur dioxide to insure ambient air quality levels required by the Environmental Protection Agency's primary and secondary standards.

Our final decision was to use Babcock & Wilcox equipment consisting of a venturi scrubber for removal of particulate matter and an absorber for sulfur dioxide removal. The schematic arrangement of this system is as per attached Exhibits C and E. The first stage of the system is a variable throat venturi scrubber for particulate removal. The second stage is a packed type of absorber using hollow plastic spheres for the packing material. Particulate matter is removed in the first stage by means of a water spray. Sulfur dioxide is removed in the second stage of the absorber section by precipitating calcium sulfate and calcium sulfite. The gas then passes through de-misters and steam reheat coils where it is reheated 25 degrees. The gas stream from the seven identical parallel modules is combined in a plenum from which it is discharged by six induced draft fans, 7000 hp each, through a 700 ft chimney.

Some 500,000 tons of limestone is expected to be used per year. This limestone, of approximately 92% calcium content, will come from local quarries and will be delivered by the supplier to a limestone hopper adjacent to the coal receiving hopper. It will be handled by the plant coal handling system for the initial part of its route to the limestone facility. Two full capacity 110-ton per hour wet ball mills will be available to grind the limestone to a fineness permitting 90% passage through a 325 mesh screen.

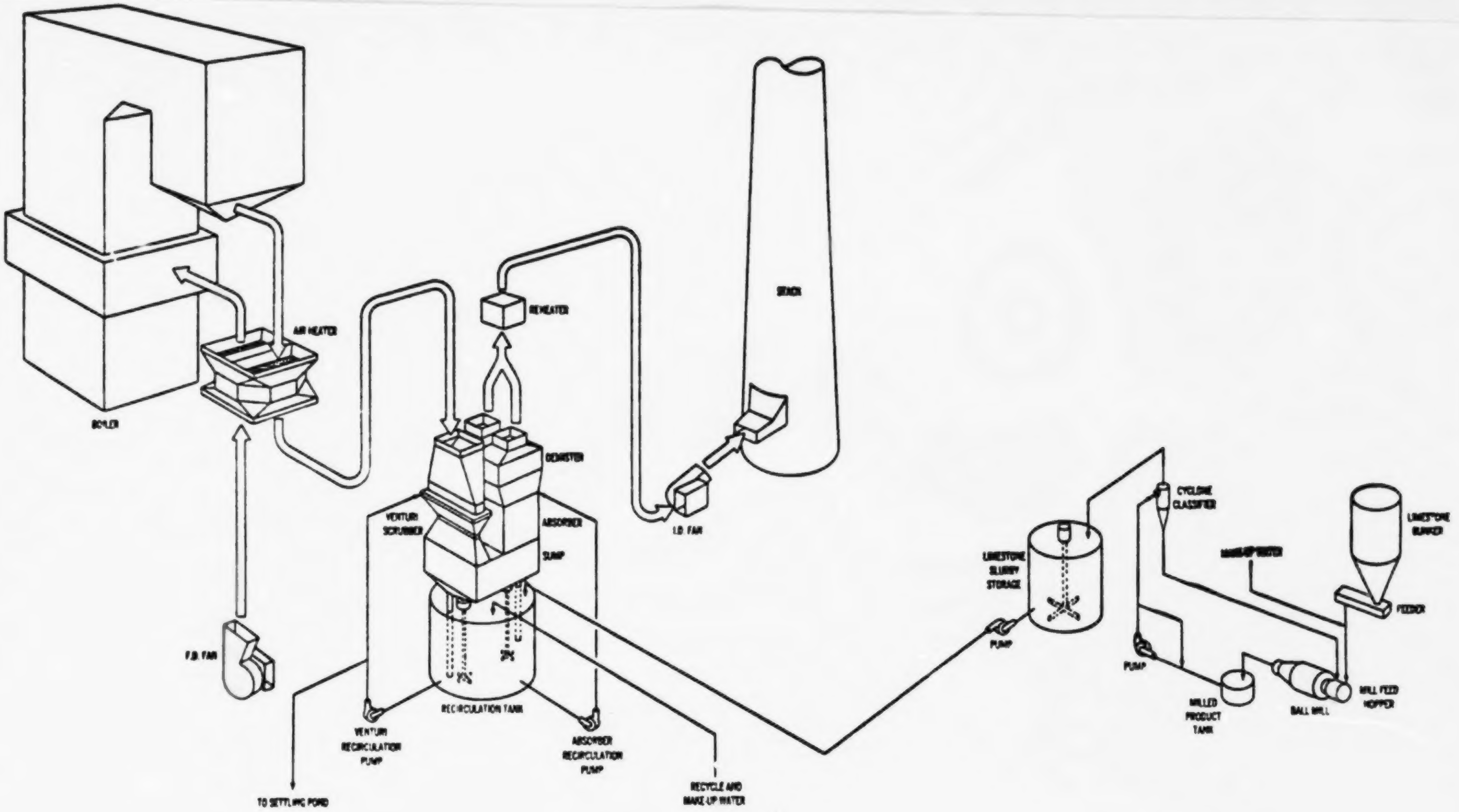
Since the SO_2 removal system will produce low pH water and since the limestone and the fly ash that accumulate in the slurry may have abrasion characteristics, the material throughout the system has to have special consideration. The venturi section will be made of #316 stainless steel and lined with 2" refractory material. The sump tanks under the venturi and absorbers will be made of carbon steel with a #316 stainless sheath bonded to the inner surface. These tanks will also have some refractory material lining in areas where abrasion may be a problem. The absorbers will be made of 316 stainless including the wire mesh baskets that contain the hollow plastic balls. The de-mister in the top of the absorber will be made of fiberglass. The steam reheat coils will be made of 5/8" diameter stainless steel tu[illegible] The breeching from the reheater to the fans and to the stack will be carbon steel. It is expected that no corrosion will take place in this area since the reheat of the gas should prevent the condensation of moisture on the walls of the breeching. The pumps and the piping in the recirculation system will be rubber lined for both corrosion and abrasion protection.

The total cost of the air quality system is estimated at $32.5 million. It is expected that 99% efficiency will be achieved for particulate matter removal and 80% for removal of sulfur dioxide. The design of the system is basically complete. Construction is underway and testing is scheduled to begin in August and September of 1972. We are certain that there are challenging times ahead for making this an effective system. We are convinced that this will be accomplished; however, recognize that the operating and maintenance costs will be substantial which, of course, will have to be added to the electric rate payers' bill.


GAS INLET
GAS OUTLET
DEMISTER
VENTURI SCRUBBER
ABSORBER
SUMP
FROM LIMESTONE SLURRY STORAGE
RECIRCULATION TANK
VENTURI RECIRCULATION PUMP
ABSORBER RECIRCULATION PUMP
TO SETTLING POND
RECYCLE AND MAKE-UP WATER

VENTURI-ABSORBER MODULE

Exhibit C



LIMESTONE SCRUBBING SYSTEM

Exhibit E

SULFUR DIOXIDE SCRUBBER SERVICE RECORD
UNION ELECTRIC COMPANY--MERAMEC UNIT 2

J.F. McLaughlin, Jr.
Union Electric Company
St. Louis, Missouri

Prepared for
Second International Lime/Limestone
Wet Scrubbing Symposium
New Orleans, Louisiana
November 8-12, 1971

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SULFUR DIOXIDE SCRUBBER SERVICE RECORD

UNION ELECTRIC COMPANY--MERAMEC UNIT 2

The following summary shows total days during which the precipitator was blanked off to direct the boiler flue gas through the sulfur dioxide scrubber. The type operation during each test period is indicated by showing the number of days the unit was either out of service, firing gas, or firing coal.

From	To	No Load	Gas Firing 50-125 MW	Coal Firing 50-55 MW	Coal Firing 100-110 MW	Total Days
9-9-68	10-5-68	4	17	--	4	25
11-11-68	12-5-68	5 1/2	--	11	9	25 1/2
2-15-69	3-2-69	8	--	6 1/2	1 1/2	16
6-16-69	6-21-69	--	1/2	1 1/2	3	5
10-3-69	10-10-69	--	--	3 1/2	3 1/2	7
11-24-69	12-22-69	2	--	6	20	28
2-16-70	3-25-70*	10 1/2	--	6 1/4	20 1/4	37
8-31-70	9-6-70	--	--	2 1/2	4 1/4	6 3/4
5-2-71	6-4-71	--	15 1/4	3 3/4	14	33
Total		30	32 3/4	41	79 1/2	183 1/4

*Unit was shut down temporarily from March 6 to March 17 but not converted to precipitator operation.

9/27/71

J.F. McLaughlin, Jr.

WILL COUNTY UNIT 1
LIMESTONE WET SCRUBBER

by
D. C. GIFFORD
COMMONWEALTH EDISON COMPANY
CHICAGO, ILLINOIS

presented at
SECOND INTERNATIONAL LIME/LIMESTONE WET SCRUBBER SYMPOSIUM
SHERATON-CHARLES HOTEL
NEW ORLEANS, LOUISIANA
NOVEMBER 8-12, 1971

Commonwealth Edison in order to gain technical understanding and to determine the economics and feasibility of sulfur dioxide removal, embarked on the installation of two separate and different facilities for the removal of sulfur dioxide from boiler flue gas.

One system is a pilot plant at our State Line Station that will produce elemental sulfur. This is a joint research project with Universal Oil Products of their sulfoxel process.

The second system is a full size limestone wet scrubber that will remove particulate and sulfur dioxide at our Will County Station, Unit 1. This is the system I will discuss. I will cover a progress status report as well as the technical aspects of this system.

In January of 1970, the existing electrostatic precipitator was found inadequate to meet the existing particulate emission standards.

Accordingly, in the spring of 1970, we contracted with Bechtel Corporation to investigate the sulfur removal systems available and to recommend a system that had the greatest chance of success.

Bechtel recommended a wet scrubber system using limestone or lime. A specification was then prepared by Bechtel and released for bid. Of the nine bidders that were solicited, only seven proposals were received. After detail study and bid evaluation with consideration of the project schedule, Babcock and Wilcox was given authorization to begin the detail engineering in September, 1970. A formal purchase order was issued in November, 1970, with a project completion deadline of December 31, 1971. This completion date was established by the Illinois Commerce Commission as part of a recent rate case.

The Babcock and Wilcox designed process is guaranteed to remove 98% of the fly ash and 76% of the sulfur dioxide, but is anticipated to remove 99% and 83% respectively. These efficiencies are based on a dust inlet loading of 1.355 grains per standard cubic foot at 70 degrees F. and burning 4% Illinois sulfur coal. In considering scrubbers, the pressure drop across a scrubber with the same dust removal capability differs greatly between a cyclone boiler with its smaller dust sizing and a pulverized fuel boiler with its larger dust sizing.

The Will County wet scrubber is being backfitted on a 163 net megawatt Babcock and Wilcox radiant cyclone boiler that was put in service in 1955.

The wet scrubber is indicated on this property plat of Will County Station.

The wet scrubber, like gaul, is divided into three parts; a limestone milling system, the wet scrubber, and the sludge disposal area.

The milling system as shown on slide 2 consists of a limestone conveyor, two 260 ton capacity limestone storage silos, two full sized Allis Chalmers wet ball mills, and a slurry storage tank. Each silo when full can supply the wet scrubber for 24 hours of operation. The limestone required should be high in calcium carbonate, above 97%. It should be noted that the reactivity of the limestone is not necessarily related to the chemical analysis of the limestone.

Each wet, ball type mill is designed to pulverize 12 tons of limestone per hour so that 95% will pass through a 325 mesh screen. The mill output product is in the form of a water slurry with 20% solids. The slurry is piped to the 4 hour capacity, 62,500 gallon slurry storage tank where it is pumped to the wet scrubber system.

The wet scrubber system is made up of two identical systems each taking half the boiler flue gas. Each system consists of two recirculation tanks, slurry recirculation pumps, a Venturi fly ash scrubber, a sump, a sulfur dioxide absorber, flue gas reheater, and ID booster fan.

For clarity I have broken the wet scrubber system into two subsystems, a gas system and a slurry system.

Slide 3 shows the flue gas path. Flue gas passes from the boiler after the precipitator and goes to the Venturi. Here the gas is forced through a pressure spray of water coming from nozzles on each side of the venturi.

The gas pressure drop through the venturi is 9 inches of water. The removal of fly ash is effected by the collision of the particles with small water droplets (the ability to collect fly ash is a function of water droplet size).

From the venturi the gas turns through the sump and then upwards into the absorber. Here the sulfur dioxide is removed as the gas at greatly reduced velocity is forced through two separate stages of plastic spheres. These spheres, coated with limestone slurry provide a wetting surface for the chemical reaction. They also act as cleaners to prevent buildup of solids. The abosrber outlet has a chevron type demister. The gas pressure drop through the absorber is 6 inches of water. Space for a third stage of plastic spheres is available if found necessary.

From the abosrber the flue gas is reheated from 128 degrees F to 200 degrees F to give the gas buoyancy and to limit condensation in the fans, ducts and existing steel brick lined stack. The bare tube reheater is divided into three sections, the first is made of 304 stainless steel, the other two sections are corten steel. Each reheater has four sootblowers to maintain tube cleanliness.

To compensate for the draft loss across the wet scrubber, an ID booster fan is used that discharges to the existing boiler ID fan. It is intended that the new booster fan maintain a zero differential across the bypass damper and that the existing ID fan will continue to control the furnace pressure.

Slide 4 shows the slurry recirculation system. There are three venturi recirculation pumps and four absorber recirculation pumps connected to their own header. Normal operation will be with each venturi and absorber system isolated from each other, but the flexibility is there to enable online pump maintenance. The sump is designed so that there is little or no mixing of the venturi and absorber recirculation flows. The fresh limestone slurry at 20% solids is added to the absorber recirculation tank where water dilutes the slurry to 8% solids. The spent or waste slurry is taken off the venturi pump discharge line.

Tank level differences are compensated by an interconnection between the two tanks. Each tank holds 42,000 gallons and provides a reaction hold up time or four minutes in the absorber recirculation tanks and six minutes in the venturi recirculation tanks. Space is available to add two more tanks to increase the hold up time to six minutes for each absorber system if the system performance characteristics dictate.

The flow of slurry to each venturi is 5800 gallons per minute and to the absorber is 8750 gallons per minute. This gives a liquid to gas ratio of 18.4 to 1 and 28 to 1 respectively.

The variable throat venturi and the three sections in the absorber allows a load range from 30 to 100% boiler load.

The waste slurry is pumped to a settling pond and all the water runoff is recycled to the wet scrubber and milling system. With our pond arrangement there could be a limited blowdown but Illinois law allows a dissolved solids limit on water discharges to the canal of only 750 parts per million. With total recycle the dissolved solids concentration is expected to be 2500 parts per million. To compound the difficulty of any blowdown, the canal water used for makeup has a concentration of 625 parts per million.

Slide 5 is a sketch of the entire system showing the milling system, venturis, absorbers, recirculation tanks, pumps, reheaters, fans, and duct arrangement.

The materials used for the construction of the system are:

Flues from the boiler to the venturi, carbon steel
The venturi, carbon steel with plasite 7122 and two inch kaocrete

The sump, corten steel with flakeline 103 and two inch kaocrete

The sump bottom, lined with firebrick

The absorber, rubber lined corten steel

Flues from absorber to reheater, corten steel with flakeline 103

Flues from reheater to the ID booster fan, corten steel

ID booster fan, corten steel housing, carbon steel wheel

The pumps, recirculation tanks, valves, and all piping in contact with slurry above six inches in diameter is rubber lined carbon steel

Any piping less than six inches in diameter is 316 L stainless steel

The power requirement for the entire wet scrubber system is nine megawatts or 5.1% of the unit gross capacity of 177 megawatts. This is nearly equivalent to the auxiliary power consumed by the rest of the unit. The eleven largest power consumers are:

Two ID booster fans, 2250 HP each

Two limestone mills, 400 HP each

Four absorber recirculation pumps, 200 HP each

Three venturi recirculation pumps, 350 HP each

The controls for the wet scrubber system are all located on a ten foot long central control board that has approximately as many instruments as the present boiler board. This new control board will allow complete start up, operation, and shut down of the mill and wet scrubber system remotely.

Slide 6 shows that the estimated cost for the system is in excess of $8 million, with equipment about $4,750,000, erection about $2,600,000, and professional engineering about $750,000. This amounts to $49 per net kilowatt hour.

The limestone cost delivered is about $5.00 per ton. Full load operation requires 15 tons per hour or 130,000 tons per year.

With sludge production anticipated at 19 tons per hour at full load, it will be necessary to dispose of 166,000 tons per year. The cost to get rid of the sludge will approach $5.00 per ton. This cost per ton would take the sludge from the pond and convert it from toothpaste consistancy to a solid, stable, non-reverting material.

The above costs related in cents per million BTU's are as follows:

Carrying charges on $8.1 million for 15 years, 11.5

Limestone, 5.0

Sludge disposal, 6.5

Manpower (one shift position), 1.0

Auxiliary power, 2.0

for a total of 26 cents per million BTUs. This total does not include maintenance or property tax.

So far I have just talked about the equipment and design. Construction presents a great many probelms both physically and schedule wise. Slide 7 shows how it was necessary to sandwich the scrubber between the boiler house and service building with a substantial canteliver. Also shown on the slide is the complexity of the duct arrangement.

Due to foundation problems the equipment erection did not start until mid May, 1971. Judicious use of overtime will allow the erection of equipment to be completed by the end of this December.

To conclude my presentation, here are some slides that I took at various stages of construction.

Figure 1

PROPERTY PLOT

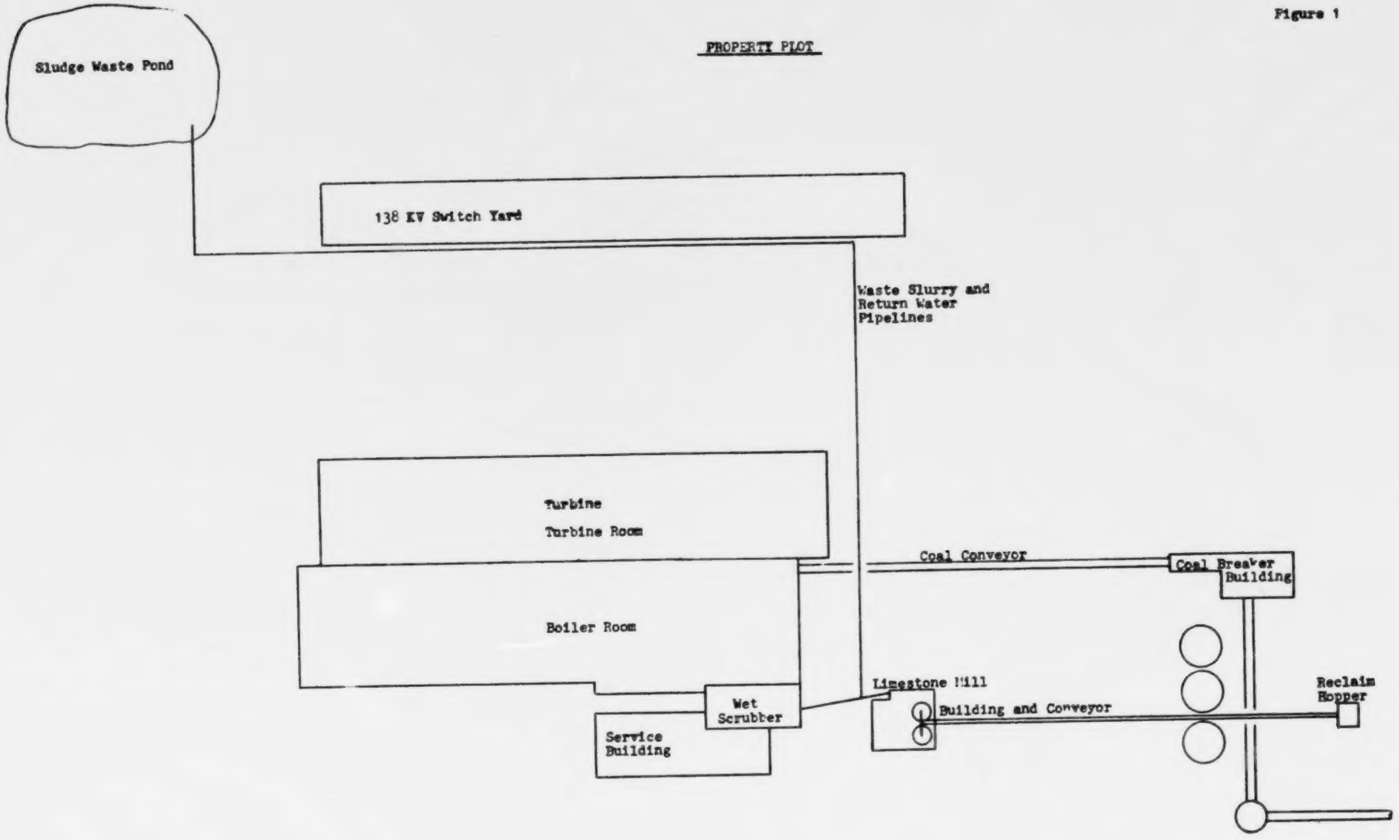
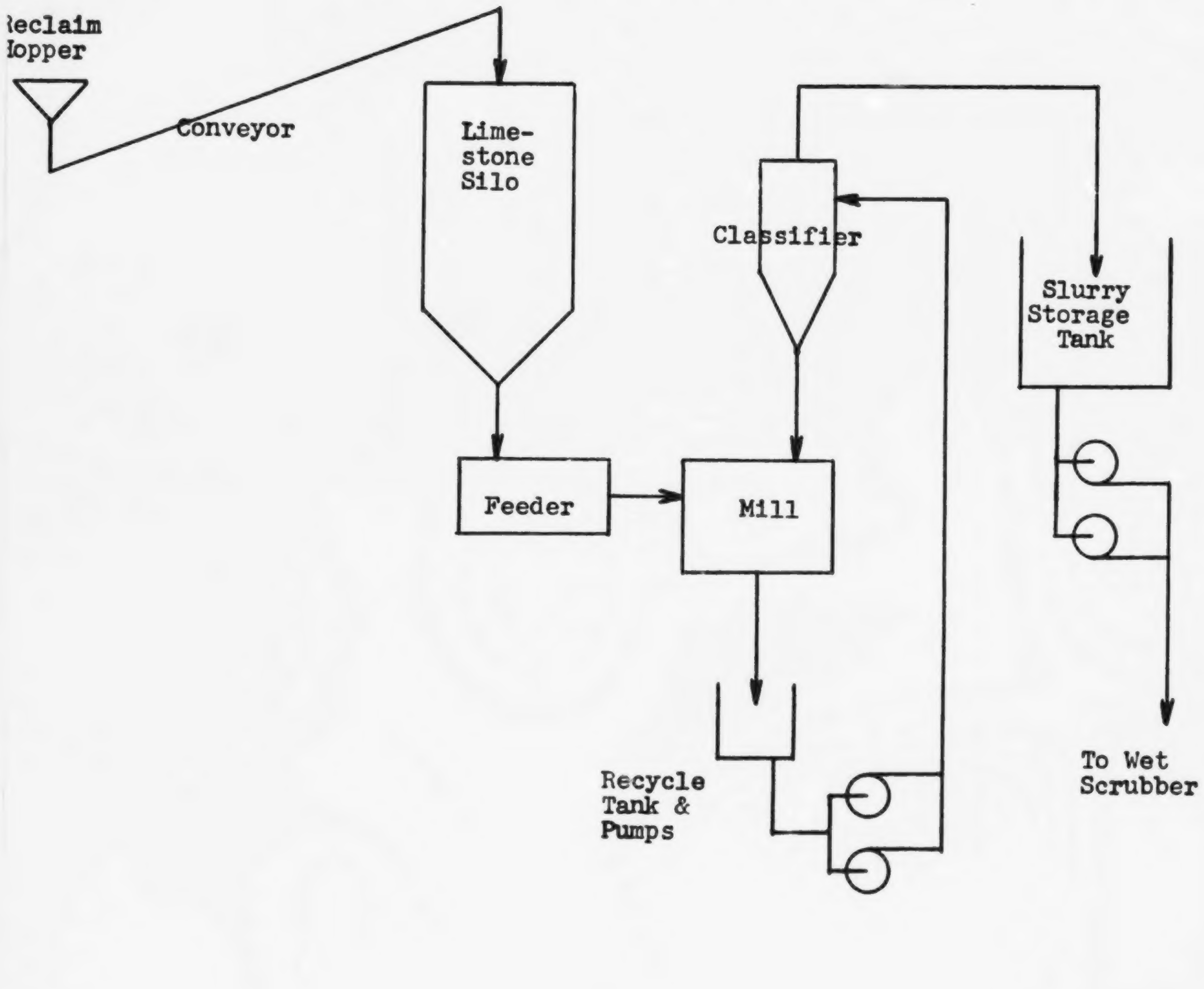


Figure 2

MILLING SYSTEM



Figure

FLUE GAS PATH

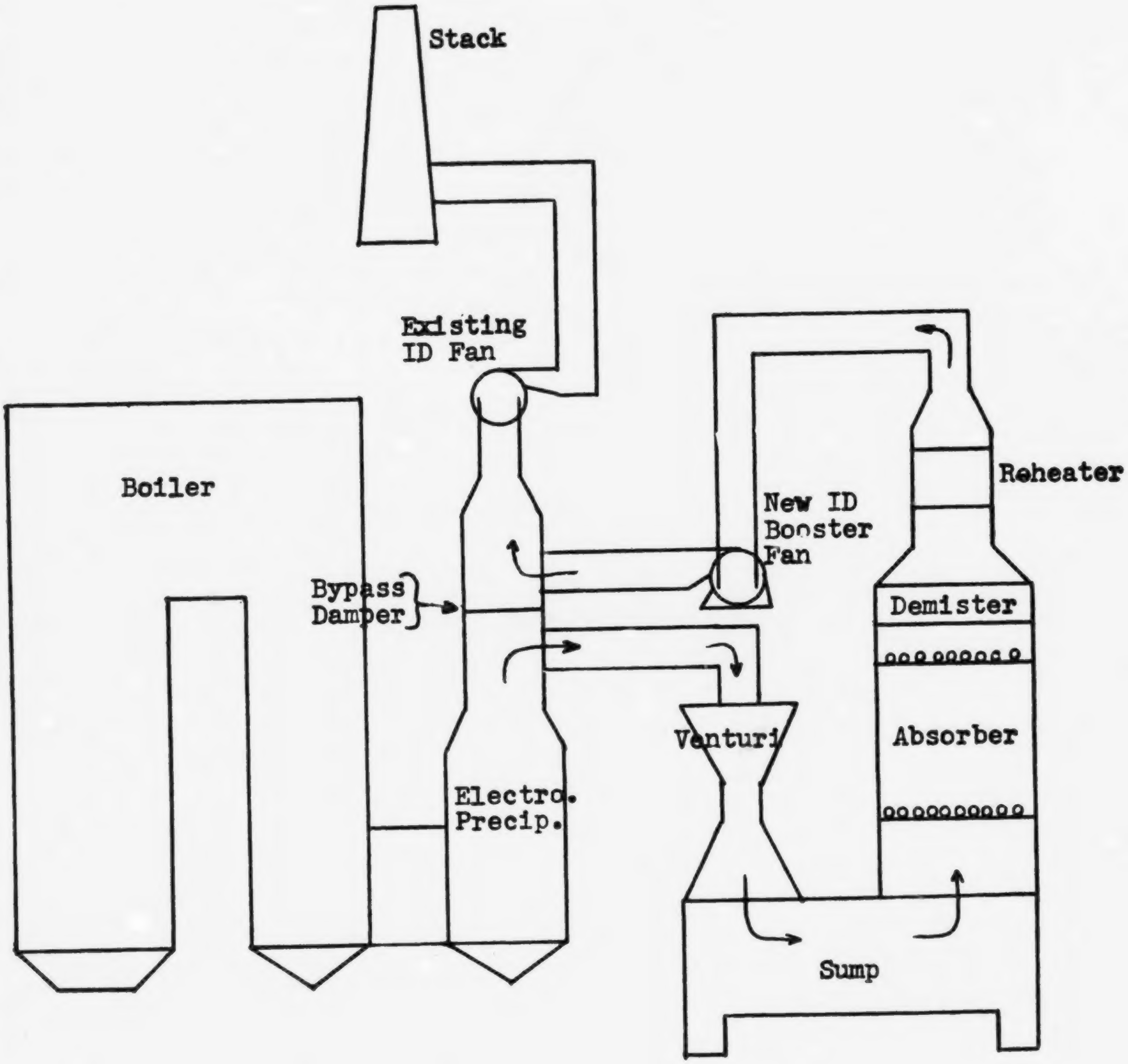
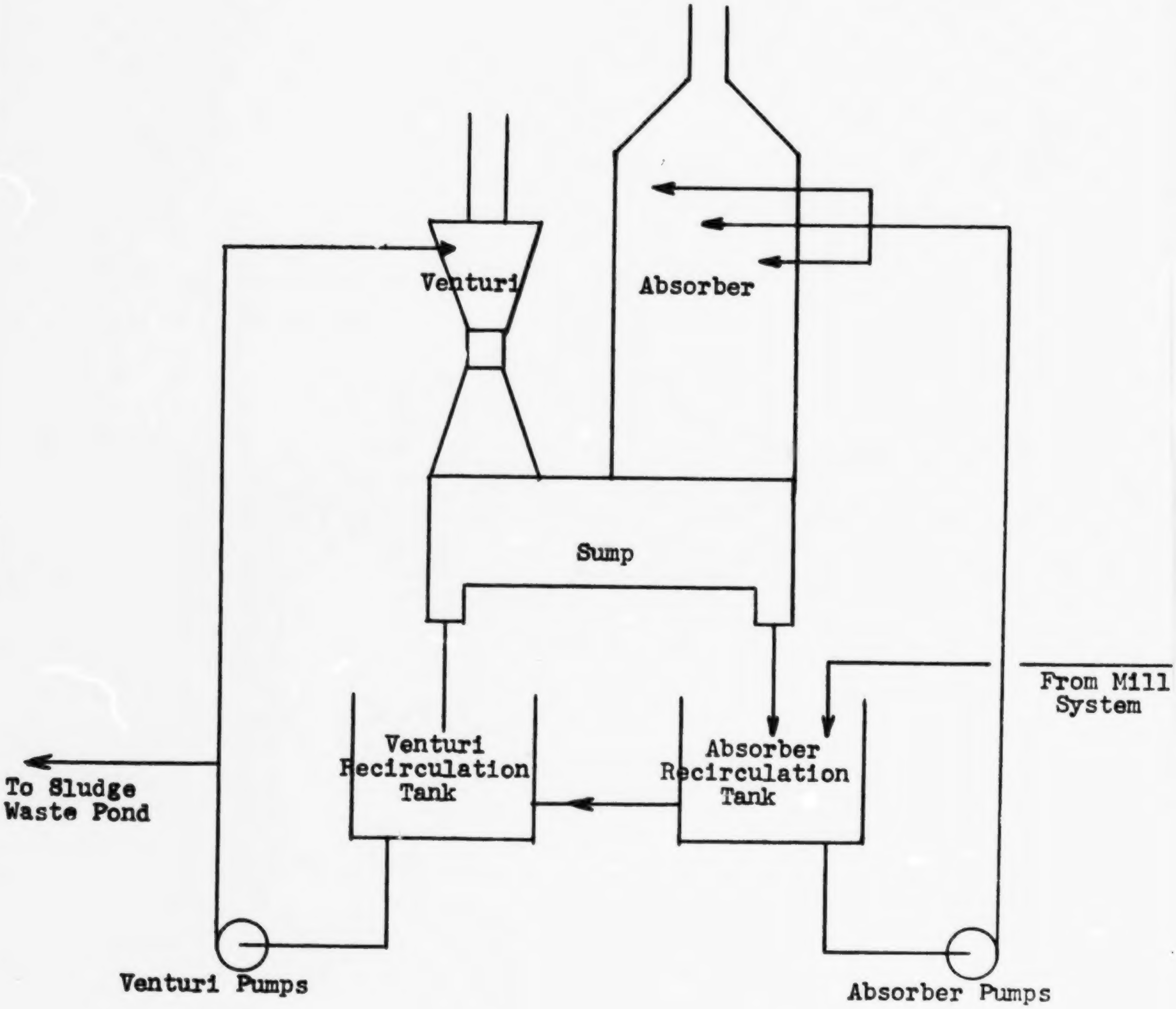
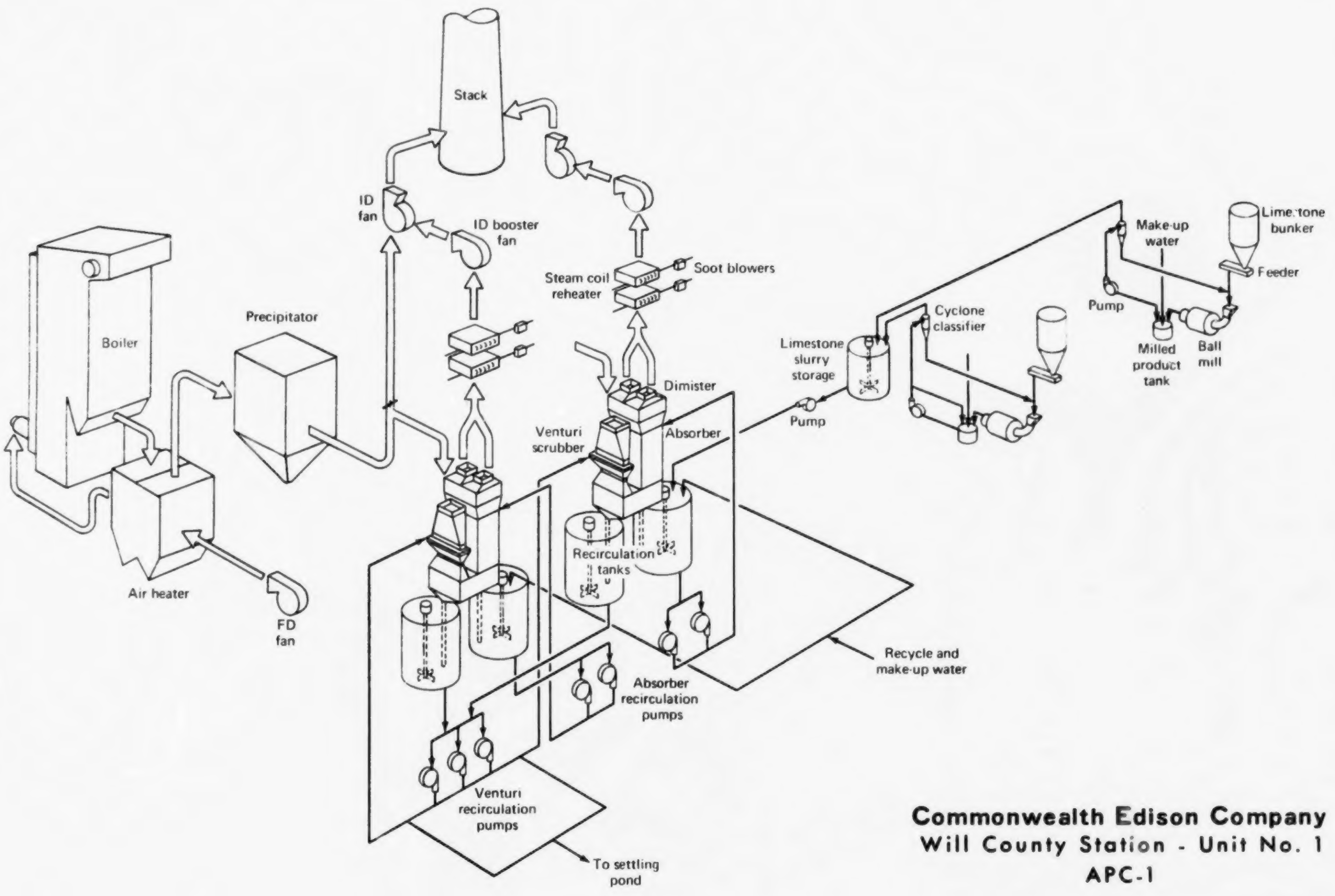


Figure 4

SLURRY RECIRCULATION SYSTEM





Commonwealth Edison Company
Will County Station - Unit No. 1
APC-1

Figure 5

Estimated Costs

Figure 6

Wet Scrubber System

Investment	
Equipment, buildings and foundations	$4,750,000
Erection	2,600,000
Professional Engineering	750,000
	$8,100,000
Operating	
Carrying charges on $8,100,000 for 15 yrs.	11.5¢/MBTU
Limestone at $5.00/ton (130,000 tons)	5.0¢/MBTU
Sludge disposal at $5.00/ton (166,000 tons)	6.5¢/MBTU
One shift position	1.0¢/MBTU
Auxiliary power	2.0¢/MBTU
	*26.0

*Note: This does not include maintenance or property tax.

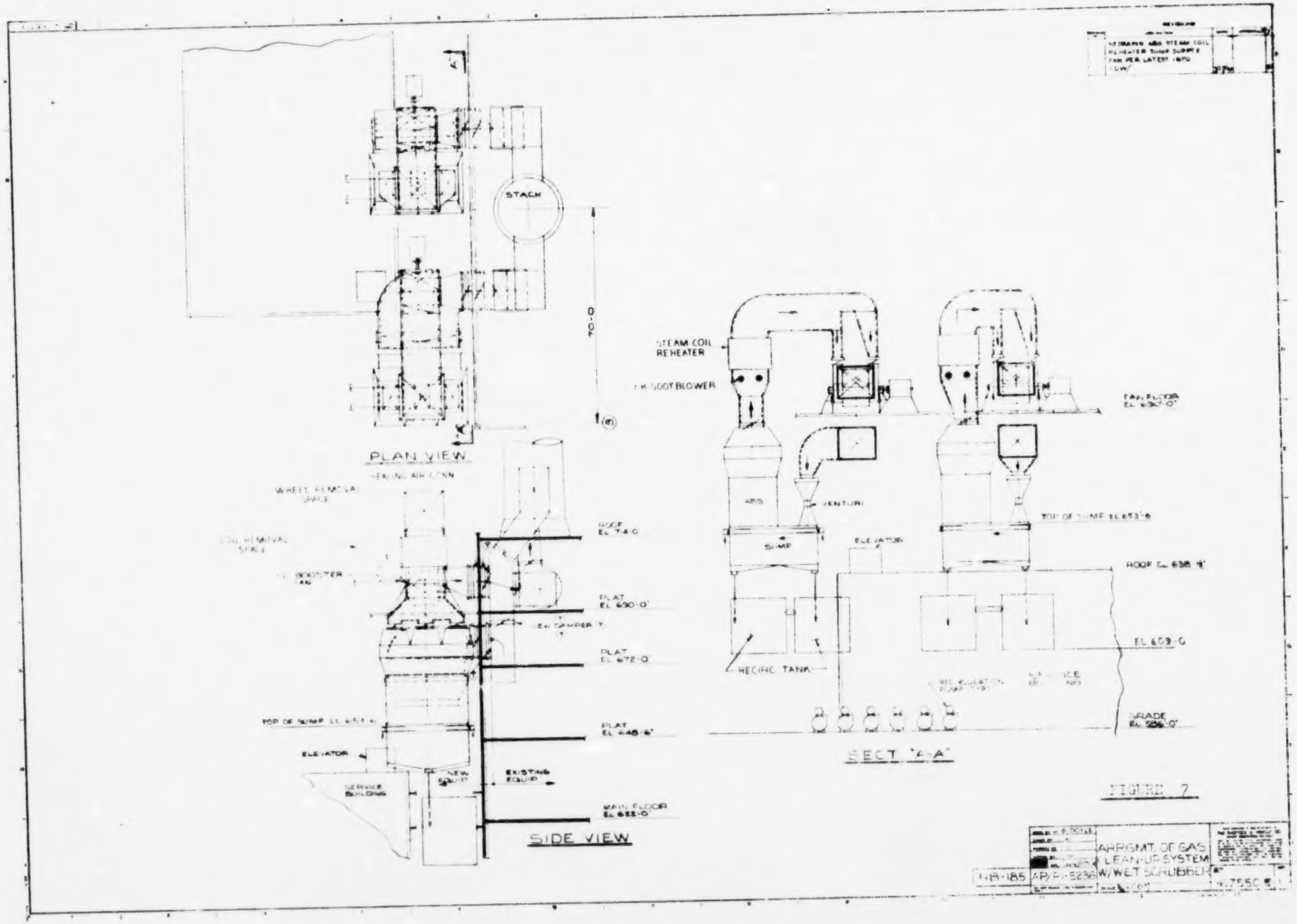

REDRAWN ABS STEAM COIL
REHEATER SUMP SUPPORT
FAN PER LATEST INFO
PLAN VIEW
STACK
40'-0"
SEALING AIR CONN
WHEEL REMOVAL SPACE
COIL REMOVAL SPACE
BOOSTER FAN
NEW DAMPER
ROOF EL 714-0
PLAT EL 690-0"
PLAT EL 672-0
PLAT EL 648-6"
MAIN FLOOR EL 622-0"
TOP OF SUMP EL 653-6
ELEVATOR
SERVICE BUILDING
NEW EQUIP
EXISTING EQUIP
SIDE VIEW
STEAM COIL REHEATER
I.K. SOOTBLOWER
ABS
VENTURI
SUMP
ELEVATOR
FAN FLOOR EL 690'-0"
TOP OF SUMP EL 653'-6
ROOF EL 638'-1"
EL 609-0
RECIRC TANK
RECIRCULATION PUMP
GRADE EL 586'-0"
SECT "A-A"
ARRGMT. OF GAS
CLEAN-UP SYSTEM
W/WET SCRUBBER
HB-185
AP/FI-5236
6.7550

FIGURE 7

A SUMMARY REPORT - CHEMICO'S COMMERCIAL SYSTEMS INSTALLATIONS AT ELECTRIC POWER GENERATING STATIONS

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Presented At
2nd International Lime-Limestone
Wet Scrubbing Symposium
New Orleans, Louisiana
November 8 - 12, 1971

hemical Construction Corporation

Pollution Control Division

A Summary Report of Chemico's Commercial Systems-Installations At Electric Power Generating Stations

H. P. Willett, Vice President Pollution Control Division
I. S. Shah, Chief, Process Engineering And Development

hemico's extensive research and development work. Bench scale, pilot plant cale and prototype scale, is aimed at developing capabilities to offer suitable olutions - both technically and economically feasible - for pollution problems of the tility industry. The major pollution problems of the utility industry are emissions of y ash, sulfur dioxide (SO_2) and nitrogen oxides (NO_x). Chemico has developed and continuing to develop technology for:

(a) Fly Ash Removal

(b) Simultaneous removal of Fly ash and SO_2 using lime - limestone throw away processes

(c) SO_2 recovery using Magnesium base SO_2 recovery process, to produce saleable products.

this presentation, we would like to summarize the various projects, one in oper- ion and the others under construction, in the utility industry, and briefly describe the portant features for each installation. The various projects are summarized in able I.

ly Ash Removal - Holtwood Station of Pennsylvania Power and Light Company

iler No. 17 is a pulverized coal fired balanced draft boiler having generating capacity 72 MW. The coal used is Anthracite, dredged from the river basin, having an ash content 17 - 20% and a sulfur content of 0.5-0.6%. The boiler was originally equipped with

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Fly Ash Removal - Holtwood Station of Pennsylvania Power and Light Company (Cont'c

mechanical collectors and electrostatic precipitator for dust collection. The scrubber system is designed to handle 358,000 ACFM of flue gas leaving the air heater at 360°F and -8" WG. This represents 80% of the total flue gas. The balance, 20% of the gas, flows through the precipitator and partially blanked mechanical collector section. The hot gases leaving the precipitator, mixes with saturated gas leaving the scrubber, thus providing a reheat of approximately 35-40°F. The mixed reheated gas is exhausted to the atmosphere through existing I.D. Fans and stack.

The liquor system consists of a thickener, recycle pump tank, and neutralization tank (to neutralize thickener underflow with lime). The underflow after neutralization is then sent to an ash pond through existing fly ash disposal pumps.

The scrubber system is designed to reduce the outlet dust loading to 0.04 grains/SCF dry when the inlet dust loading is 4.5 grains/SCF day or less. In case the inlet dust loading is higher than 4.5 grains/SCF day, the scrubber system will provide 99% efficiency.

The scrubber system is successfully meeting the guaranteed performance, even though the ash content of coal has increased from the design value o 17% (4.5 gr/SCFD) to 38% (10 gr/SCFD).

Fly Ash Removal-Four Corners Station - Arizona Public Service Company

Units No. 1, 2 and 3 are pulverized coal fired balanced draft boilers having generating

Fly Ash Removal - Four Corner Station - Arizona Public Service Company(Cont'd)

capacity of 175 MW, 175 MW and 225 MW respectively. The coal used contains 28.8% ash and 0.6% sulfur. The boilers were originally equipped with mechanical collectors. Each of the three boilers will be equipped with two scrubbers, I. D. Fans, (wet) mist eliminators, and reheaters. Each scrubber handles a flue gas volume of 407,000 ACFM at 340°F and -10" W. G., in the case of units 1 and 2, and a flue gas volume of 515,000 ACFM at 340°F and -10" W. G., in the case of unit 3. The flue gas from units 1 and 2 are discharged to the atmosphere through one common existing stack whereas unit 3 has its own existing stack. Adjustable throat mechanism are provided to maintain constant dust removal efficiency at varying loads.

A common liquor system, for all three boilers, consists of thickeners, pump tanks and existing ash pond. The thickener overflow, and liquor from ash pond are returned to scrubber system.

The scrubber system is designed to provide an outlet dust loading of 0.4 grains/SCFdry with an inlet dust loading of 12 grains/SCFdry. The flue gas is reheated by 20°F to avoid condensation of water vapor in the high velocity stack. The system will be in operation before the end of this year.

Fly Ash Removal - Dave Johnson Station, Unit 4, Pacific Power and Light Company

Unit no. 4 is a new pulverized coal fired balanced draft boiler having generating capacity of 360 MW. The coal fired has an ash content of 16% and sulfur content

Fly Ash Removal - Dave Johnson Station, Unit 4, Pacific, Power and Light Company(Con)

0. 4%. The total flue gas of 1, 487, 100 ACFM at 270°F and -12" W. G, and having dust loading of 12 grains/SCF dry, leaving the air heater is handled by three scrubbers, three wet I. D. Fans, and one common low velocity wet stack. The saturated flue gas is not reheated. The bleed liquor from the scrubber system is pumped to an ash plant, and cleared liquor from the plant is returned to the scrubbers. Adjustable throat mechanisms are provided in each scrubber, to maintain constant pressure drop to achieve constant dust removal efficiency at varying boiler loads.

The scrubber system is designed to provide outlet dust loadings of 0. 04 grains/SCFdry provided the inlet dust loading is 12. 0 grains/SCFdry or less. The plant is under construction and scheduled for start-up early in 1972.

SO_2 Recovery - Mystic Station, No. 6 Unit, Boston Edison Company, and Essex Chemical Company's Acid Facility at Rumford, Rhode Island

Unit No. 6, rated at 155 MW generating capacity is equipped with air heaters, electrostatic precipitator (de-energized when burning oil fuel), two induced draft fans and a stack. At 155 MW rating, the flue gas volume leaving the I. D. Fans is 440, 000 ACFM at 300°F and +1" W. G. The SO_2 loading is 1410 ppm (by volume, dry gas basis). The flue gas leaving the two I. D. Fans enter the two new F. D. Fans, and one Venturi Type SO_2 absorber. SO_2 is absorbed by MgO slurry in the absorber, forming a slurry of $MgSO_3$, $MgSO_4$ and unreacted MgO. The bleed from absorber is sent to a centrifuge, to produce a cake containing approximately 5% surface moisture.

SO_2 Recovery - Mystic Station, No. 6 Unit, Boston Edison Company, and Essex Chemical Company's Acid Facility at Rumford, Rhode Island (Cont'd)

The centrifuged cake is then dried in a drier by removing both crystalline and surface water. The dry product is stored in an existing fly ash silo and then trucked away to Essex Chemicals sulfuric acid facility at Rumford, Rhode Island. The dry product containing $MgSO_3$, $MgSO_4$ and MgO is calcined in a calciner, to produce SO_2 rich (12 - 16%) flue gas, and regenerate MgO. The flue gas after proper cleaning, enters the sulfuric acid plant to produce 98% H_2SO_4 acid.

The regenerated MgO is returned by truck to Mystic Station of Boston Edison, for reuse in the absorber. Make up MgO will be added to the system at Boston Edison.

The SO_2 recovery process plant will reduce the inlet SO_2 concentration of 1410 ppm in the boiler flue gas to less than 150 ppm which is equivalent to burning less than 0. 3 percent sulfur content fuel oil.

Approximately 50 tons/day of crystal $MgSO_3$, $MgSO_4$ and MgO will be produced at the power plant. The recovered sulfur dioxide from the power plant stack flue gas will be equivalent to the entire feed requirement of the 50 tons/day sulfuric acid plant at Rumford, Rhode Island. The crystals will be shipped by truck only five days a week and only during the 8 hour day shift. At the acid plant, approximately 20 tons/day. of MgO will be regenerated.

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SO$_2$ Recovery - Mystic Station, No. 6 Unit, Boston Edison Company, and Essex Chemical Company's Acid Facility at Rumford, Rhode Island (Cont'd)

The plants at Mystic Station and Essex Chemical are under construction and scheduled for start-up before the end of 1971.

Fly Ash and SO$_2$ Removal - Phillips Station of Duquesne Light Company

At the Phillips station, there are 6 boilers having a total generating capacity of 387 MW. Each of the boiler is a pulverized coal fired balanced draft unit, and is presently equipped with mechanical collector-precipitator and separate stack. The coal burnt has 21% ash and 2.3% sulfur.

The flue gas leaving the air heater from each boiler enters a manifold. The total flue gas in the manifold is 2,190,000 ACFM at 362°F and -22" W. G., and the dust loading and SO$_2$ loading are 5.9 Grains/SCFdry and 1370 ppm. This total volume of flue gas is handled by four scrubbing trains, each consisting of first stage scrubber, wet I. D. Fan, and a mist eliminator.

A common reheater and common stack are provided for all the scrubbing trains. One scrubbing train also includes a second stage absorber in place of the mist eliminator. In this two stage scrubber-absorber, simultaneous fly ash and SO$_2$ will be removed using lime as absorbing agent. The other trains will remove only fly ash using water as scrubbing liquor. The bleed from each scrubber is sent to an ash pond, and if found necessary, additional lime will be used to neutralize the

Fly Ash and SO_2 Removal - Phillips Station of Duquesne Power and Light Company(Cont'

total bleed. The clear liquor from the ash pond is returned to scrubber.

To maintain pressure drop across the scrubber throat, to attain constant dust removal efficiency at varying load conditions, the venturi scrubbers are provided with adjustable throats. As the load decreases, the throat area is reduced by closing the throat, and as the load increases the throat area is increased

The system is designed to provide an outlet dust loading of 0.04 grains/SCFdry, when the inlet dust loading does not exceed 5.9 grains/SCFdry. The outlet SO_2 concentration from one scrubber train will be 274 ppm or less. Design and engineering work is in progress, and the plant is scheduled for start up during February 1973.

Fly Ash Removal - Elrama Station of Duquesne Light Company

At the Elrama station, there are 4 boilers, having a total generating capacity of 494 MW. All the boilers are pulverized coal fired balanced draft units, and are presently equipped with mehcanical collector-precipitator. The coal is similar to that used at Phillips Station.

The flue gas leaving the air-heater from each boiler enters a manifold. The total flue gas in the manifold is 2,211,000 ACFM at 304°F, and -22" W.G. The inlet dust loading and SO_2 concentration are 7.32 grains/SCFdry and 1570 ppm. Five

Fly Ash Removal - Elrama Station of Duquesne Power and Light Company (Cont'd)

scrubbing trains will handle the total gas flow, and each train consists of a scrubber, wet I. D. Fan, and mist eliminator. A common reheater and common new stack are provided for all the scrubbing trains. All scrubbers are provided with adjustable throats to maintain efficiency at varying loads. At this plant, initially only fly ash will be removed using water as scrubbing liquor. The bleed from scrubbing system is sent to the ash pond, and clear liquor from pond is returned to scrubber. The system is designed to provide an outlet duct loading of 0.074 grains/SCFdry, provided the inlet dust loading is 7.32 grains/SCFdry or less. The plant is scheduled for start up during February 1973.

Dickerson Station - Potomac Electric Company

The unit no. 3 of the Dickerson Station is a pulverized coal fired balanced draft boiler rated at a generating capacity of 195 MW. The coal fired has an ash content of 20% and a sulfur content of 3.0%. The boiler is presently equipped with mechanical collector-precipitator system for dust removal.

Fifty percent of the total gas flow will be treated in the prototype scrubber-absorber system, where the fly ash is removed in the first stage using water as scrubbing liquor The cleaned flue gas then enters the absorber where SO_2 is removed using MgO slurry as absorbing liquor. The slurry of $MgSO_3$, $MgSO_4$ and MgO is centrifuged, the cake is dried in the drier. The dry crystals are then trucked to an acid facility of Essex chemicals, where upon calcination, MgO is regenerated, and flue gas

Dickerson Station - Potomac Electric Company (Cont'd)

rich in SO_2 is produced to make 98% H_2SO_4 acid. Approximately 50 tons/day of acid will be produced.

The ductwork is so arranged that the flue gas either before the precipitator or after the precipitator can be withdrawn. The flue gas volume will be 295,000 ACFM at 259°F and -11.0"W. G., and the dust loading and SO_2 concentration are 5.95 Gr/SCF dry and 1850 ppm respectively. The system will provide an outlet dust loading of 0.03 Gr/SCF dry, and an outlet SO_2 concentration of 185 ppm or less.

An adjustable throat mechanism will be provided to maintain constant efficiency at varying loads. Approximately 15°F reheat will be provided using off gases from the dryer. At present, engineering and design is in progress and the plant is scheduled for start up in 1973.

Fly Ash and SO_2 Removal At a Power Generating Station In Japan

A 155 MW generating station burning pulverized coal having 20% ash and 3% sulfur, in a balanced draft boiler is presently equipped with mechanical collectors-precipitator for dust removal. A flue gas volume of 451,000 ACFM at 277°F and 0" W. G., having a dust loading of 0.25 Gr/SCF dry, and SO_2 concentration of 2350. ppm will be handled in one two stage scrubber train. The gas volume represents 75% of the total flue gas. A 50°F reheat will be provided using fuel oil burners.

Fly Ash and SO_2 Removal At a Power Generating Station In Japan (Cont'd)

Carbide sludge will be used for simultaneous SO_2 and fly ash removal in a two stage venturi scrubber system, including a delay tank. The bleed from the scrubber system will be pumped to the ash pond, and clear liquor from the ash pond returned to the scrubber system.

The scrubber system which handles flue gas leaving the existing precipitator will provide 90%+SO_2 removal and an outlet dust loading of 0.025 grains/SCFD. The plant is under construction and is scheduled for start up during March 1972. This plant is designed for initial disposal consumed alkali, but for future conversion to manufacture gypsum.

Summary

Chemico designed systems to date include four plants for fly ash removal using water as scrubbing liquor, one plant each for simultaneous removal of fly ash and SO_2 using lime slurry and carbide sludge, and two SO_2 recovery plants using MgO slurry process, one each for coal fired and oil fired generating stations. Chemico designed systems will handle a total flue gas volume of 10,090,100 ACFM resulting from a total generation capacity of 2293 MW. Chemico systems designed to date will remove 4320 Tons/day of fly ash and 400 Tons/day of SO_2, from flue gases, and thus help reduce air pollution and clean the air.

TABLE I: SUMMARY OF CHEMICO's COMMERCIAL SYSTEM INSTALLATIONS

STATION AND COMPANY	LOAD MW NO. OF BOILERS NO. OF SCRUBBER TRAINS	FLY ASH AND/OR SO2	THROWAWAY OR RECOVERY	SCRUBBING LIQUOR	INLET LOADINGS DUST, GR/SCFD SO_2, PPM	OUTLET LOADINGS DUST, GR/SCFD SO_2 · PPM	SPECIAL FEATURES	GAS VOLUME ACFM TEMP. OF STATIC PRESSURE "WG"
Hottwood Pennsylvania Power and Light	72 One One	Fly Ash	Throwaway	Water	4.5	0.045	Reheat using hot flue gas cleaned precipitator dry I. D. Fan.	358,000 360 -8.0
Four Corners Arizona Public Service Company	575 Three Six	Fly Ash Now SO_2 Later	Throwaway	Water	11.9 - 12.3	0.04	20°F reheat using steam. Adjustable throats to maintain efficiency at varying loads. Wet I.D. Fans.	2,658,000 340 -10.0
Dave Johnson Pacific Power & Light	360 One Three	Fly Ash Now SO_2 Later	Throwaway	Water	12.0	0.04	No reheat, low velocity wet stack. Wet I.D. Fans. Adjustable throats.	1,487,100 270 -12.0
Mystic Station Boston Edison and Essex Chemicals	155 One One	SO_2	Recovery	MgO Slurry	1410	Less than 150	Prototype on oil fired generating unit, 15°F reheat using dryer off gases. SO_2 converted to $MgSO_3$ (50tons/day) and then to H_2SO_4 acid (50 tons/day) at Essex Chemicals. Dry F. D. Fans	440,000 300 +1.0
Phillips Station Duquesne Power & Light Company	387 Six Four	Fly Ash Now SO_2 in one train only	Throwaway	Water Time Slurry	5.9 1370	0.04 274 or less	20°F reheat using oil burners. Adjustable throats.	2,190,000 362 -22.0
Elrama Station Duquesne Power & Light Company	494 Four Five	Fly Ash Now SO_2 Later	Throwaway	Water	7.32 1570	0.074	20°F reheat using oil burners. Adjustable throats.	2,211,000 304 -22.0
Dickerson Station Potomac Electric Co.	95 One(50%) One	Fly Ash and SO_2	Recovery	Water MgO Slurry	5.95 1850	0.03 185 or less	Prototype on coal fired generating unit 15°F rehat using dryer off gases. Recovered SO_2 as H_2SO_4 acid. Wet I. D. Fan. Adjustable Throat mechanism.	295,000 259 -11.0
Utility in Japan	155 One Two	Fly Ash and SO_2	Throwaway	Carbide Sludge	0.25 2350	0.025 235 or less	Carbide Sludge for SO_2 removal. 50°F reheat using oil burners.	451,000 277 atm.

Total MW = 2,293
Total Gas Volume = 10,090,100
Tons/day, Fly Ash Removed = 4,320
Tons/day, Sulfur Dioxide = 400

PROBLEMS RELATED TO SCALING IN LIME/LIMESTONE WET SCRUBBING

A.V. Slack, Chairman

Participants:

A.V. Slack and J.D. Hatfield
Bela M. Fabuss
Joan B. Berkowitz
J.R. Martin
Philip S. Lowell

SUMMARY

PROBLEMS RELATED TO SCALING IN LIME/LIMESTONE WET SCRUBBING

Second International Lime/Limestone Wet Scrubbing Symposium
New Orleans, Louisiana
November 8-12, 1971

Participants: A. V. Slack, Chairman
B. M. Fabuss
J. Berkowitz
A. L. Plumley
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P. S. Lowell

SUMMARY

One of the major problems in removing SO_2 from waste gases by lime/limestone slurry scrubbing is scaling in the scrubber and other slurry handling equipment. Although study of the problem dates back to work in England in the 1930's, much remains to be learned about the problem--particularly in regard to the effect of differing conditions among the units producing the SO_2-laden waste gas.

The mechanisms involved in scrubber scaling are complex, much more so than for scaling of boilers and desalination equipment. Among the design and operating factors to be considered are (1) amount of SO_2 absorbed per unit of slurry passed through the scrubber, (2) content of calcium sulfite and calcium sulfate crystals in the recirculated slurry, (3) degree of desupersaturation accomplished outside the scrubber before return of the slurry, (4) pH levels at various points in the circuit, (5) scrubber design as related to tendency of solids to settle out of the slurry onto surfaces, (6) scrubber design as related to the scouring effect of the slurry, (7) degree of oxidation in the scrubber, and (8) point of lime introduction into the circuit.

Scaling can result from deposition of calcium sulfate, calcium sulfite, or calcium carbonate--although carbonate scaling is rare. Calcium sulfate is the usual scaling species but calcium sulfite is often encountered, particularly when lime is the absorbent.

The consensus is that lime gives more scaling than limestone, but no conclusive reasons for the difference have been advanced. The generally lower pH in limestone systems seems to be a factor, at least in regard to sulfite scaling. At the present level of development, lime systems must be operated with blowdown (dilution with water) or at low pH (less than the stoichiometric amount of lime) to reduce scaling to an acceptable level.

Closed-loop operation (no blowdown to watercourses) is feasible with limestone but careful attention to operating conditions is essential to avoid scaling. For adequate SO_2 removal, the slurry circulation rate and slurry solids content must be much higher for limestone scrubbing than for lime; since this should also reduce scaling, it may be that the particular level of operating variables required for good SO_2 removal with limestone is the reason for limestone superiority in regard to scaling.

The driving force for scaling is supersaturation. The formula developed in the early English work for avoiding scaling was limiting the degree of supersaturation developed in the scrubber to a level low enough to avoid crystallization on scrubber surfaces; homogeneous crystallization on sulfite and sulfate crystals was promoted, however, by carrying a large surface area of such crystals in the slurry. The supersaturation developed in the scrubber was then released in delay tanks before return of the slurry to the scrubber.

The limiting upper value in the range of supersaturation that can be tolerated is that at which bulk nucleation takes place in the solution even in the presence of seed crystals. In recent work it has been determined that this level (for calcium sulfate) is about 1.3 for the nonstoichiometric $Ca^{++}/SO_4^{=}$ ratio in the scrubber solution. (Supersaturation is defined here as $^{a}Ca^{++}\,{}^{a}SO_4^{=} / KspCaSO_4$, where a is activity and Ksp is the solubility product constant.) The critical level for calcium sulfite has not yet been determined.

Data from recent successful pilot plant operation (nonscaling) indicates a supersaturation level of 1.19 at the scrubber outlet, well below the 1.3 critical level. The value decreased to 1.02, near the saturation level, in the delay tanks before return to the scrubber. Sulfite supersaturation was much higher--8.15 at the scrubber outlet and 6.49 returning to the scrubber--indicating that the critical level is much higher than for sulfate.

The effects of scouring by the slurry or mechanical accumulation of carbonate or sulfite crystals on surfaces followed by knitting together or converting to sulfate have not yet been adequately evaluated. The composition of the scrubber surface does not seem significant from tests so far, and little is known regarding the effect of additives or of ionic strength.

Further study is needed on all phases of the scaling problem. In the meantime, the best course appears to be (1) use of limestone rather than lime, (2) high recirculation rate, (3) high solids content in slurry, (4) adequate delay time, and (5) use of scrubbers of the spray or mobile-bed type. Since both of these scrubber types have major drawbacks--low mass transfer rate and excessive packing wear, respectively--it may be better to use a very open type of fixed packing. Recent work with a set of wire screens as packing has given excellent absorption, relatively low wear, and no apparent scaling.

REMOVAL OF SULFUR DIOXIDE FROM STACK GASES BY SCRUBBING WITH LIMESTONE SLURRY: OPERATIONAL ASPECTS OF THE SCALING PROBLEM

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ABSTRACT

Scaling in lime-limestone scrubbing for SO_2 removal is a very complicated process; much more is involved than the simple crystallization of calcium sulfate from solution in scaling of boilers and desalination equipment.

The possible effects of the following process variables on scaling are discussed.

- Degree of desupersaturation in the surge tank.
- Amount of SO_2 absorbed per unit volume of liquor recirculated.
- Use of limestone rather than lime as the absorbent.
- Various factors related to scouring, such as slurry rate, slurry velocity, solids content of slurry, particle size of solids, scrubber type (e.g., mobile-bed vs fixed packing), and impingement angle between slurry and surface.
- Factors affecting tendency of solids to silt onto surfaces, including surface roughness and presence of transverse surfaces that catch solids.
- Point of lime introduction into the scrubber circuit.
- Presence of fly ash in slurry.
- Degree of oxidation in scrubber.
- Nature of scrubber surfaces (e.g., plastic vs steel) in regard to strength of bond developed between crystal nucleus and surface.

- Use of additives that weaken the bond between crystal and surface.

At the present state of the art, the most effective measures for avoiding scaling appear to be (1) adequate delay time for desupersaturation in surge tank, (2) use of limestone rather than lime, (3) high recirculation rate (needed anyway with limestone for good SO_2 removal), (4) elimination of surfaces that collect solid particles from the slurry, (5) high solids content in slurry, and (6) use of scrubbers designed to maximize the scouring action.

REMOVAL OF SULFUR DIOXIDE FROM STACK GASES BY SCRUBBING WITH LIMESTONE SLURRY: OPERATIONAL ASPECTS OF THE SCALING PROBLEM

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Because of marketing problems, the power and smelter industries are generally turning to throwaway processes--production of a waste solid--as a means of coping with the SO_2 emission problem. Lime or limestone is the preferred absorbent since only a very low cost material can be considered when there is no return from sale of product.

Since the use of limestone as sorbent in a dry system has been generally unpromising, most of the current effort is centered on absorption of the SO_2 by a slurry of lime or limestone. Although this has shown considerable promise, and is the method that has been selected by most of the power and smelter companies that are planning to install full-scale SO_2 removal facilities, there are some major technical problems that remain unsolved. The main one of these is scaling, that is, growth of an adherent crystalline deposit on scrubber surfaces that eventually causes shutdown because of interference with gas or liquid flow.

In this paper, the effect of operating factors, both chemical and physical, on the scaling problem will be reviewed. The material presented is based mainly on small-scale and pilot plant studies carried out at TVA.

The Basic Problem

The reaction of SO_2 with CaO or $CaCO_3$ in a scrubbing operation produces mainly crystalline $CaSO_3 \cdot 0.5H_2O$. There is some dissolved sulfite, however; the equilibrium concentrations of the various species produced vary with pH, which depends on whether CaO or $CaCO_3$ is the absorbent and on whether a countercurrent or backmixed scrubber is used. For CaO and a backmixed scrubber, which gives the highest pH, the principal dissolved sulfite species are HSO_3^-, $SO_3^=$, and $CaSO_{3(aq)}$ with $CaSO_{3(aq)}$ preponderant. With $CaCO_3$ and a countercurrent scrubber, which gives the lowest pH, the HSO_3^- concentration is higher and the $SO_3^=$ lower.

If oxygen is present in the gas, as it is in most situations, there will be some oxidation of dissolved sulfite during passage of the solution through the scrubber. Part of the resulting sulfate remains in solution, the amount depending on several factors. The remainder crystallizes as $CaSO_4 \cdot 2H_2O$, which in most cases is the species that causes scaling--by crystallizing on equipment surfaces.

Solubility data for sulfite and sulfate are given in Table I.[1] Of more importance in regard to scaling, however, is the tendency of both calcium sulfate and sulfite to supersaturate. Lessing[2], in development of the ICI-Howden process, found that $CaSO_4 \cdot 2H_2O$ would supersaturate, in a simulated solution, by about four times the saturation concentration. In recent TVA pilot plant tests, the indicated degree of supersaturation at the scrubber outlet has averaged about 1.8 to 1.9 times saturation concentration. The degree of calcium sulfite supersaturation has appeared to be even higher; these results will be checked in further tests.

TABLE I

Effect of pH on Solubility[a] in the System $CaO-SO_2-SO_3-H_2O$ at 50°C (122°F)

	Parts per million		
pH	Ca	SO_2[b]	SO_3[c]
7.0	675	23	1,320
6.0	680	51	1,314
5.0	731	302	1,260
4.5	841	785	1,179
4.0	1,120	1,873	1,072
3.5	1,763	4,198	980
3.0	3,135	9,375	918
2.5	5,873	21,999	873

[a] Solution saturated with $CaSO_3 \cdot 0.5H_2O$ and $CaSO_4 \cdot 2H_2O$.

[b] Sulfite.

[c] Sulfate.

The basic operational factors involved in scaling are illustrated by Figure 1. The flowsheet shown is for a countercurrent scrubber and for CaO or $CaCO_3$ introduction into the recirculation tank. Variations from this include (1) backmixed or cocurrent scrubbing and (2) injection of limestone into the boiler, in which case the resulting CaO enters the scrubber with the gas.

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[1] Slack, A. V., Falkenberry, H. L., and Harrington, R. E. "Sulfur Oxide Removal from Waste Gases: Lime-Limestone Scrubbing Technology." Paper presented at 70th National Meeting, American Institute of Chemical Engineers, Atlantic City, New Jersey, August 29-September 1, 1971.

[2] Lessing, R. J. Soc. Chem. Ind. 57, 373-88 (Nov. 1938).

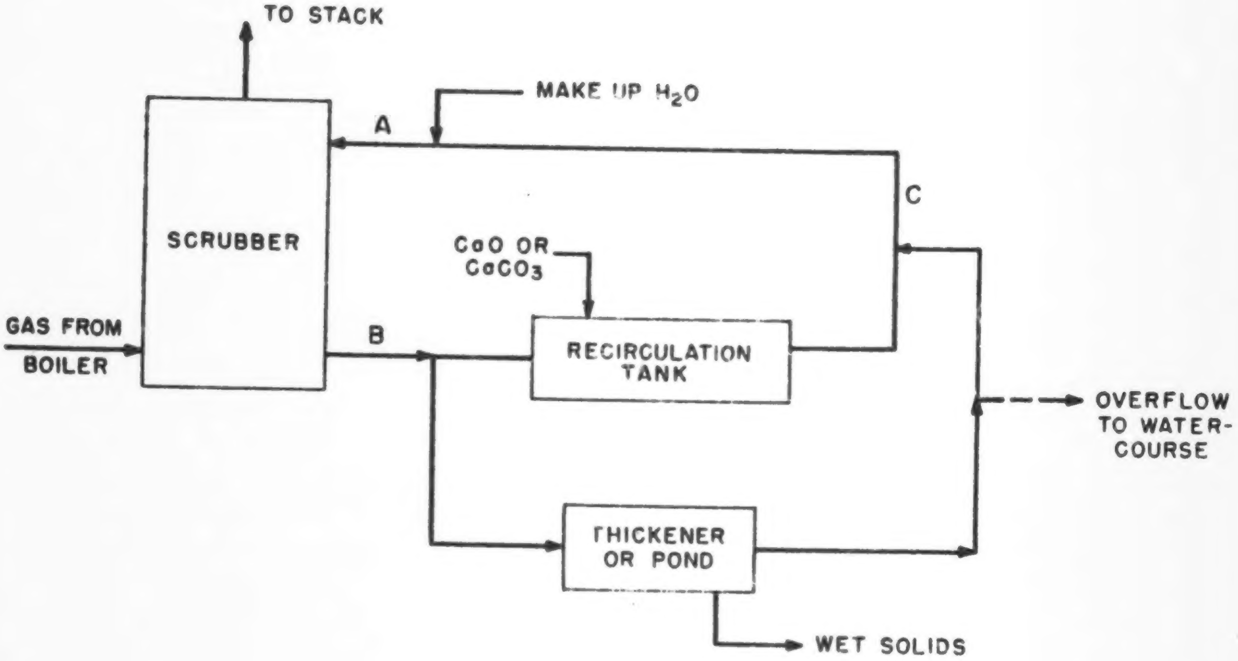

FIGURE 1

Flow System Involved in Scaling

Operation of the system will be discussed in terms of the slurry composition at points A, B, and C in the recirculation loop. At A the slurry contains the solid species $CaSO_3 \cdot 1/2H_2O$, $CaSO_4 \cdot 2H_2O$, and $CaCO_3$ (or CaO). The liquid phase hopefully is unsaturated with sulfite-sulfate species because of the water addition just before A and insufficient time for solid sulfite and sulfate to resaturate the solution.

In the scrubber, SO_2 is absorbed and forms various dissolved sulfite species. At the inlet pH involved in limestone scrubbing (about 6.0), the main species present, HSO_3^-, is in equilibrium with a much smaller amount of $SO_3^=$. The pH decreases as the solution flows down through the countercurrent scrubber, thereby bringing Ca^{++} into solution. This causes the solubility product of Ca^{++} and $SO_3^=$ to be exceeded (under normal scrubbing conditions) with the result that a driving force for $CaSO_3 \cdot 0.5H_2O$ crystallization is developed. Crystallization does not necessarily occur, however, because the $CaSO_3 \cdot 0.5H_2O$ tends to supersaturate. Even a mild tendency to supersaturation may have a major effect because the rapid passage of the solution through the scrubber leaves little time for nucleation and crystal growth.

Even if crystallization takes place it can occur on the surface of calcium sulfite crystals already present in the slurry (homogeneous crystallization) or on other solids ($CaSO_4 \cdot 2H_2O$, $CaCO_3$, fly ash; heterogeneous crystallization). If the driving force for crystallization becomes high enough, however, the capacity of these mechanisms to hold sulfite in a harmless form will be exceeded and crystallization on scrubber surfaces will occur. This is usually expressed as "critical degree of supersaturation," that which must not be exceeded if scaling is to be avoided.

The decrease in pH as the solution flows through a countercurrent scrubber increases the amount of total sulfite species present at saturation. Hence the solution can hold more sulfite in the lower part of the scrubber without exceeding the critical degree of supersaturation.

Calcium sulfate also tends to supersaturate in the scrubber and also has a critical degree of supersaturation. However, since its solubility decreases with pH (when the solution is saturated with sulfite) there is no advantage from the pH drop in the scrubber.

At point B the solution is supersaturated with both calcium sulfite and sulfate. In the recirculation tank the pH rise from CaO or $CaCO_3$ addition reduces sulfite solubility and promotes desupersaturation. The retention time in the tank and in the thickener (or pond) also aids in desupersaturation by allowing time for crystallization to take place. The objective is to have the solution at or near saturation at point C. Although unsaturation would obviously be desirable, such a goal seems impracticable except by water addition close to the scrubber inlet. Unsaturation without water addition could be achieved only by removing all the sulfite and sulfate crystals and then crystallizing further by usual crystallization techniques; there are several process and economic considerations that make this course undesirable.

Lessing proposed the following equation for rate of scaling.

$$K = \frac{(C_1 - C)/(C - C_2)}{pt}$$

where C = concentration of $CaSO_4 \cdot 2H_2O$ at time t

C_1 and C_2 = initial and final $CaSO_4 \cdot 2H_2O$ concentrations

p = amount of sulfate crystals

The value of K, about 1.5 in the ICI work, depends somewhat on the type of sulfate crystals; small, thin ones have more surface area and therefore are more effective in dissipating supersaturation than are blocky ones.

Use of Diluting Water

Of the various process steps available for reducing scaling, addition of water to the slurry entering the scrubber is one of the more effective. For example, if the slurry is diluted by 20%, i.e., addition of 20 gal water per 100 gal of slurry liquid phase, the capacity of the resulting liquid to take up SO_2 in the scrubber is increased by about 35% on the basis of solubility alone (assuming that without the water addition the saturated liquid phase can absorb only that amount resulting from a drop in pH from 6.0 to 5.5 in the scrubber). In addition, the benefit of supersaturation is increased in proportion to the volume of water added.

The main disadvantage of diluting water is that liquid must be removed from the system (blowdown) to maintain the liquid volume in the system at a constant level. Eventually this blowdown must be drained to a watercourse, carrying with it dissolved sulfite and sulfate plus soluble constituents introduced by the limestone and the boiler gas (Mg, Cl, Na, K). The water pollution aspects of this are discussed in another of the papers in this symposium ("Potential Water Quality Problems Associated with Lime/Limestone Wet Scrubbing for SO_2 Removal from Stack Gas" by James S. Morris).

Since there are some unavoidable losses of water from the system, a certain amount of water can be added without need to blow down part of the scrubbing solution. A water balance for typical scrubber conditions is shown in Figure 2. The toal allowable makeup, 0.76 ton water per ton of coal burned, is quite small in comparison with the amount of liquid recirculated. The makeup is equivalent to a blowdown of only about 1.0%.

Reduction in pH

There is an increasing body of evidence to the effect that reduction of pH in the scrubber decreases scaling. No conclusive explanation for the effect appears to have been advanced.

When CaO is used, the reduction in pH can be accomplished by cutting back on the $CaO:SO_2$ ratio to less than stoichiometric. This reduces SO_2 absorption, of course; the question then is whether the reduction in SO_2 absorption required to avoid scaling will make it difficult to meet SO_2 emission regulations. No data appear to have been reported on the point. Dilution with water can be combined with pH reduction, of course, to improve absorption without incurring scaling.

The beneficial effect of low pH may be associated with the deposition of solid $CaCO_3$ that can occur at high pH. In small-scale continuous tests at TVA, use of $Ca(OH)_2$ rather than $CaCO_3$ as the feed material (in countercurrent scrubbing) resulted in rapid deposition of $CaCO_3$ in the upper part of the scrubber near the slurry inlet. The deposit also contained $CaSO_4 \cdot 2H_2O$; it may be that $CaCO_3$ was converted to $CaSO_4 \cdot 2H_2O$ in place. In the work reported by Lessing, the accumulated scale contained as much as 18% $CaCO_3$, which also indicates the possibility of $CaCO_3$-$CaSO_4$ conversion on the scrubber surfaces.

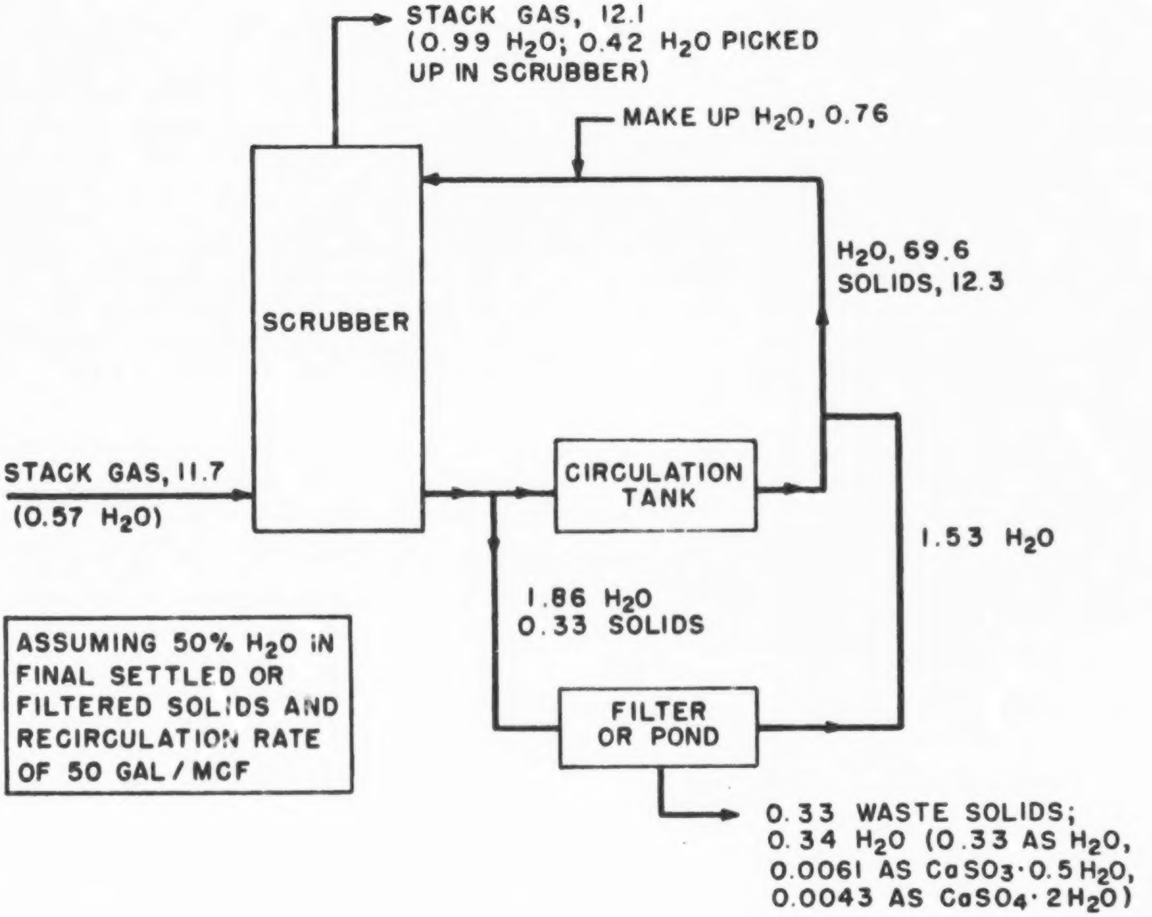
STACK GAS, 12.1
(0.99 H_2O; 0.42 H_2O PICKED UP IN SCRUBBER)
MAKE UP H_2O, 0.76
H_2O, 69.6
SOLIDS, 12.3
SCRUBBER
STACK GAS, 11.7
(0.57 H_2O)
CIRCULATION TANK
1.53 H_2O
1.86 H_2O
0.33 SOLIDS
ASSUMING 50% H_2O IN FINAL SETTLED OR FILTERED SOLIDS AND RECIRCULATION RATE OF 50 GAL/MCF
FILTER OR POND
0.33 WASTE SOLIDS;
0.34 H_2O (0.33 AS H_2O, 0.0061 AS $CaSO_3 \cdot 0.5H_2O$, 0.0043 AS $CaSO_4 \cdot 2H_2O$)

FIGURE 2

Water Balance for SO_2 Removal from Stack Gas by Scrubbing with Limestone Slurry

Quantities are tons per ton of coal burned

The use of $CaCO_3$ instead of CaO, which also gives a lower pH level in the system, has generally reduced scaling. In the TVA tests mentioned above, there was no deposition when $CaCO_3$ slurry was used instead of $Ca(OH)_2$.

The pronounced effect of pH on sulfite solubility may also be a factor. A given reduction in pH in a low pH range (say, from pH 6 to 4) gives more increase in sulfite solubility than a similar reduction at a higher level (say, from pH 9 to 7).

Solids Content of Slurry

Much of the available data on scaling comes from the early work in England on the ICI-Howden process[1,2,3,4]. One of the more important variables in this work was the content of calcium sulfite and sulfate crystals in the recirculating slurry; the concentration specified for the full-scale unit constructed at the Fulham station was 3 to 5% each of calcium sulfite and calcium sulfate.

Although a large number of sulfite-sulfate crystals circulating in the scrubber loop provides surface on which dissolved sulfite and sulfate tend to crystallize preferentially, this alone does not seem to be sufficient for preventing scaling. In the ICI work it was necessary to adjust other factors also to get nonscaling operation. In TVA pilot plant tests, scaling occurred even though $CaCO_3$ slurry was used and the solids content of the slurry was about 15%.[5]

Desupersaturation in Surge Tank

Another variable found important in the ICI work was retention time of the slurry before return to the scrubber. It was considered necessary to provide enough time to dissipate the supersaturation developed in the scrubber, since it is apparent that any degree of supersaturation at point C in Figure 1 reduces the capacity of the solution for absorbing SO_2 in the scrubber without incurring scaling.

ICI specified a retention time of about 2.5 minutes in the recirculation tank. The effects of delay time and crystal concentration on supersaturation, as reported by Lessing, are shown in Figure 3. Conclusive

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[1] Lessing, R. J. Soc. Chem. Ind. 57, 373-88 (Nov. 1938).

[2] Rees, R. L. J. Inst. Fuel XXV (148), 350-57 (March 1953).

[3] Hewson, G. W., Pearce, S. L., Pollitt, A., and Rees, R. L. Soc. Chem. Ind. (London), Chem. Eng. Group, Proc. 15, 67-99 (1933).

[4] Pearson, J. L., Nonhebel, G., and Ulander, P. H. N. J. Inst. Fuel VIII (39), 119-156 (February 1935).

[5] However, the species distribution was 5.0% $CaSO_3 \cdot 0.5H_2O$ and 1.5% $CaSO_4 \cdot 2H_2O$ (remainder ash), and therefore the amount of $CaSO_4 \cdot 2H_2O$ may not have been sufficient. Moreover, the excess of calcium sulfite may have been harmful; Lessing pointed out that the presence of sulfite crystals can cut in half the beneficial effect of sulfate crystals on sulfate desupersaturation.

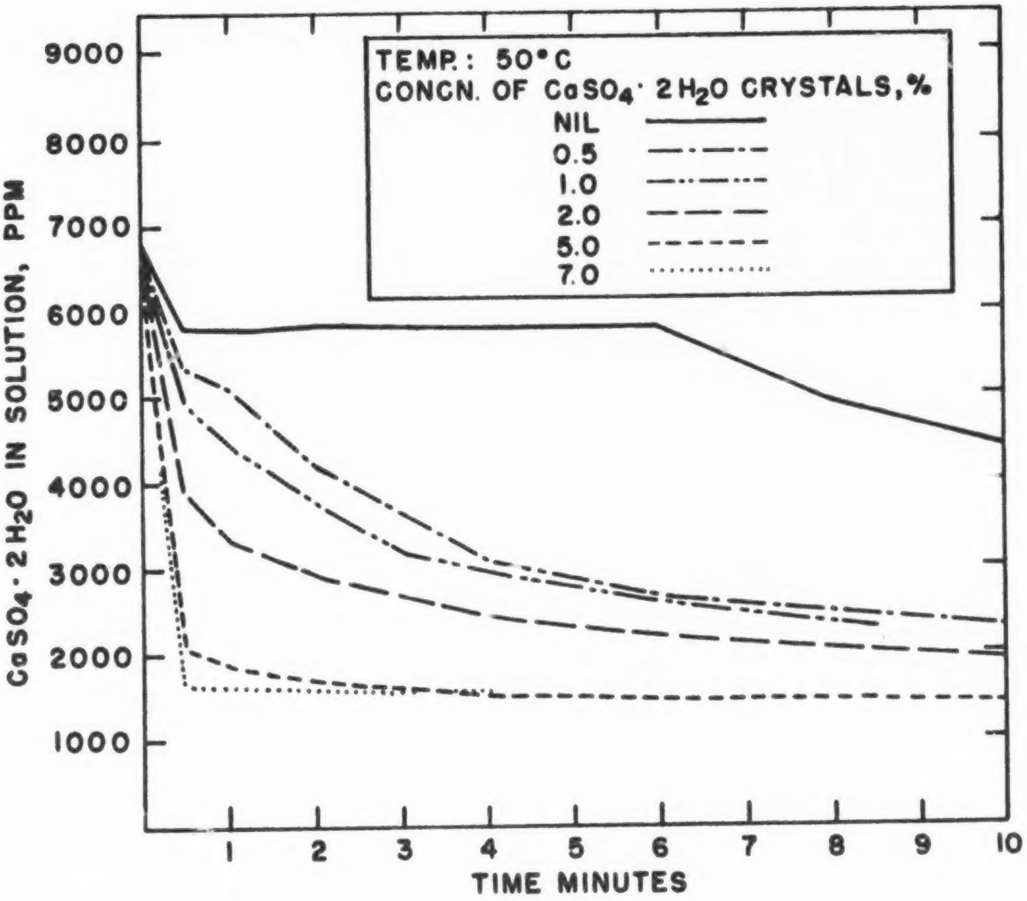

FIGURE 3

Effect of Delay Time on Supersaturation of $CaSO_4 \cdot 2H_2O$

data on the effectiveness of surge tank retention time have not been obtained yet in the TVA work. In the small-scale tests with $Ca(OH)_2$, the combination of 1% solids and 1-minute delay time gave rapid scaling. Increase to 3% solids and 10-minute retention reduced the scaling and further increase to 4% solids (still with 10-min retention) essentially eliminated the problem. In the pilot plant, the delay time is about 10 minutes (at 50 gal/Mcf circulation), which should be adequate for desupersaturation. There is some indication, however, that the solution returning to the scrubber is still supersaturated in regard to both sulfate and sulfite; further data will be obtained in an effort to resolve the question.

It should be noted that the rise in pH in the hold tank due to the dissolution of CaO or $CaCO_3$ results in a much lower solubility of calcium sulfite (Table I) and consequently a very high degree of supersaturation can be developed even if the solution entering the hold tank is only saturated with calcium sulfite. For example, if the pH rises from 5.0 to 6.0 in the hold tank and the entering solution at pH 5.0 is saturated with calcium sulfite, the 302 ppm of SO_2 in the incoming stream is about six times the saturation amount in the returning stream (at pH 6.0) to the top of the scrubber. Unless sufficient delay time is permitted to precipitate the excess sulfite, it is not surprising that the returning solution will likewise be supersaturated. The extent to which the solution entering the hold tank is supersaturated will serve to increase further the supersaturation in the solution returning to the top of the scrubber. The opposite effect is obtained with calcium sulfate; a pH rise from 5 to 6 in the hold tank increases the sulfate solubility (Table I) by about 5%. However, since the resulting decrease in supersaturation is small, delay time is necessary to dissipate the supersaturation before return of the solution to the scrubber.

Slurry Circulation Rate

A further process variable emphasized in the ICI work was amount of slurry circulated per unit of SO_2 absorbed. After optimization of surge tank retention time and solids content of the slurry, the critical degree of supersaturation in the scrubber could be determined. From this the amount of slurry circulation necessary to avoid exceeding the critical value was calculated. For the inlet SO_2 concentration involved in the ICI tests (about 1000 ppm SO_2), the circulation rate required was about 130 gal per Mscf of gas.

This amount of circulation is almost intolerable for the situation in the eastern part of the United States, where the high sulfur content of the coal produces an inlet SO_2 concentration two to three times that in the British work. For an inlet SO_2 content of 3000 ppm, which is not uncommon, the required slurry rate would be about 400 gal/Mcf to give a liquor:SO_2 ratio similar to that used by ICI. Capital and operating costs for such a pumping load would be extremely high.

This objection would not hold for the western part of the United States, where the sulfur content of the coal is quite low, for example, 0.6%. For 0.6% sulfur, the slurry rate equivalent to the ICI practice would be only about 50 gal/Mcf.

In use of CaO in this country, the general practice has been to operate with a relatively low L/G (gal/Mcf) because good SO_2 absorption can be obtained with CaO at low liquor rate (on the order of 10-30 gal/Mcf).

Hence scaling has been promoted by the low liquor:SO_2 ratio. For $CaCO_3$, which is much less reactive than CaO, it has been necessary to use higher L/G (on the order of 40-60) to get good absorption, which is favorable to reduction of scaling. This is another factor, in addition to lower system pH, that makes $CaCO_3$ a better absorbent in regard to scaling.

One possibility would be to use two or more scrubbing stages with separate recirculation circuits. Enough delay time could be designed into each circuit to desupersaturate the solution so that the sulfite-sulfate make in each circuit would not be large enough to cause precipitation and scaling. Such a system would be expensive but might solve the problem.

Erosive Effect of Slurry

There is some evidence that the erosive or scouring effect of the slurry may be a very important factor in scaling. In the TVA pilot plant work, severe scaling was encountered when stack gas was scrubbed with $CaCO_3$ slurry in a crossflow scrubber. There was no significant scaling, however, in spray and mobile-bed scrubbers. The slurry circulation rate and slurry solids content were somewhat higher in these tests, but the main difference was the intense scouring effect of the high velocity sprays in the spray scrubber and the bouncing spheres in the mobile bed--as compared with the relatively slow flow of slurry through the crossflow. The thin spines of $CaSO_4 \cdot 2H_2O$ formed on the crossflow packing are shown in Figure 4. It would be expected that the erosive action in the other two scrubbers would break off such spines as fast as they formed.

Even without solid particles in the liquor, it would be expected that high velocity flow of liquid past surfaces would discourage adherence of nuclei in the formative stage. This point was emphasized in the ICI work.

There are numerous factors that may affect the magnitude of the scouring effect.

1. Slurry pumping rate obviously is important, but has generally been fixed more by SO_2 removal requirement than by other considerations.

2. Slurry velocity. In a spray scrubber a relatively high liquor velocity from the spray nozzles is necessary for good spray distribution. Velocity probably is lowest in the fixed packing type. Data on effect of liquor velocity are not available.

3. Solids content of the slurry should be as high as practicable. However, the 12 to 15% used in the TVA and ICI work for other reasons (mainly to provide crystal surface) may be as high as should be attempted. The slurry not only scours crystals away from surfaces but also erodes the surfaces themselves. TVA

FIGURE 4

Calcium Sulfate Scale on Scrubber Packing has under way a test program aimed specifically at the erosion problem. This work may indicate that a lower solids content should be used to avoid excessive erosion.

4. Particle size of solids will also be varied in the TVA tests, since small particles should not be as erosive as large ones. They may also be less effective in removing scale.

Silting

One of the more puzzling aspects of scaling is the effect of silting, that is, the accumulation of solids on scrubber surfaces by mechanical means--either by settling onto transverse surfaces or into crevices or by fine particles being caught bodily on rough surfaces. If calcium sulfate crystals are accumulated in this way, dissolved sulfate should crystallize on them as it does on crystals in the bulk slurry. The difference is that nucleation on surfaces is bypassed when crystals accumulate on surfaces by mechanical means; crystallization on the accumulated crystals can cement them together and onto the surfaces, thus providing an additional mechanism for scaling.

Calcium carbonate and calcium sulfite crystals can accumulate on scrubber surfaces in the same way. Calcium carbonate is not stable in the system except at high pH. In reacting with the solution, however, it may become converted in place to calcium sulfite or sulfate and thus cause scaling. Calcium sulfite can also form a relatively stable form of scale although the scale found in TVA tests has been mainly sulfate.

No data appear to be available on the effect of silting. In the TVA crossflow scrubber work, relatively loose deposits of $CaCO_3$ formed in the packing, presumably by silting. Calcium sulfate also formed but it is not clear whether or not the silting contributed to the sulfate scale formation. However, the fact that the spray and mobile-bed scrubbers, in which silting would not be likely, did not scale is a possible indication that silting is a factor. Further work on the point appears desirable.

Degree of Oxidation in Scrubber

It seems logical that the "make" of sulfite and sulfate in the scrubber, per volume of solution, should have a major effect on the degree of scaling; as noted earlier, this was the basic consideration in the ICI work. The limited data on the point from U.S. work are confusing. In the recent TVA tests, only 10 to 20% oxidation of sulfite occurred in the scrubber (as indicated by the solid phase composition) yet the scale was mainly sulfate.

Work by others has produced sulfite scaling, however, even at a degree of overall oxidation on the order of 50%. It is not clear what makes the difference and whether it is better to promote or inhibit oxidation as far as scaling is concerned.

It is obvious that much more study is needed in this area, since there are ways to change oxidation rate if such a change would be helpful. Data are needed on the relationship between sulfite and sulfate in regard to (1) supersaturation driving force needed under various conditions to initiate nucleation, (2) activation energy of nuclei formation, (3) strength of bond in adherence to surfaces, (4) rate of crystal growth after nucleation, and the effect of increasing amounts of homogeneous surface for growth, and (5) effect of other dissolved constituents and of ionic strength.

Nature of Surfaces

The type of construction material and condition of the surface may be significant. ICI adopted wood packing and pointed out that corrosion roughening of steel surfaces promoted scaling. Today wood is not favored as a packing material and steel surfaces likely will be covered with rubber or plastic to reduce corrosion and erosion. In the TVA pilot plant tests, scale grew well on polypropylene packing and in small-scale work scale formation occurred on glass.

It does not seem likely that type of construction material will be a major factor in preventing scaling. However, it may be important enough to be a trade-off alternative in determining the most economical solution to the problem.

Use of Additives

In the desalination field various additives have been proposed for reducing or avoiding scaling. Several mechanisms can be considered, including nucleation inhibition, weakening the bond between crystal and surface, formation of films that alter surface properties, and alteration of crystal habit to change crystal growth pattern. A major drawback is that such additives are likely to be expensive and that they will be lost from the system with the liquor in the discarded wet solids. However, the cost might be justified if a major benefit resulted. Experimental work is indicated since experience in the desalination field will not likely be applicable because of the wide differences between the two systems.

Summary

Although a considerable amount of experience has accumulated on scaling in lime-limestone systems, much remains to be learned regarding the mechanisms involved and the best way to arrive at a reliable and economical method for eliminating the problem. The ICI-Howden formula of adequate retention time in the recirculation tank, high crystal content in the slurry, and high recirculation rate per unit of SO_2 absorbed does not appear applicable to high-sulfur coals because of the extremely high pumping load required; however, it may be usable for low-sulfur coal. Since the ICI method was developed from basic chemical considerations, there is no obvious way to improve on it from the standpoint of process chemistry except for using limestone instead of lime, which, for some reason as yet not clearly identified, reduces scaling considerably.

There are, however, some mechanical factors that may be helpful. With slurry composition and scrubber design aimed at producing an intense scouring effect, it appears that scaling can be controlled at slurry recirculation rates no higher than those required for good SO_2 absorption.

The next step should be optimization of the system to give the most economical combination of conditions. This will require a considerable amount of research and development on the quantitative effect of the various factors and on the basic mechanisms involved.

CALCIUM SULFATE SCALING

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CALCIUM SULFATE SCALING

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Distillation processes are usually regarded as the most effective means of producing potable water from saline or brackish water. The evaporative desalination is often hampered by the formation of calcium sulfate scale on the heat transfer surfaces. This scale may be deposited at low temperatures in the form of gypsum, at high temperatures as hemihydrate and may undergo transformation to anhydrite.

Figure 1 shows a summary of the solubility curves for these three modifications. It can be seen that both the anhydrite and the hemihydrate show a strong inverse solubility. Figure 2 shows pilot and demonstration plant data of the Office of Saline Water projects plotted on this diagram. It clearly indicates that scale-free operation was frequently achieved well above the anhydrite solubility curve and even in some instances above the hemihydrate solubility curve.

Figure 3 shows several sea water heating runs at a series of heating rates and on two different surfaces, stainless steel and an epoxy resin. Figure 4 shows a series of experiments when the supersaturation was achieved by evaporation at a constant temperature. Finally, Figure 5 summarizes these data giving two sets of precipitation curves superimposed on the calcium sulfate solubility diagram. In summary, this work clearly shows that the precipitation limits and scale formation depend on the operating conditions of the unit. Concentration of sea water by non-boiling heat transfer permits operation at significantly higher supersaturations than by boiling heat transfer. The effect of other variables such as the heating surface materials, additives, and heating and evaporation rates was slight. Scaling was controlled primarily by kinetic factors, determined by the residence time of the solution in the unit.

In applying these considerations to lime scrubbing of stack gases, let us take a look at the equilibrium concentrations of the ions and molecules in the system. We are dealing here only with the dissolved ions. Figure 6 shows the calculated concentration of the ions in the solution at equilibrium.

If we consider that scaling occurs by calcium sulfate precipitation and not by calcium sulfite or hydroxide deposition, this can occur only at high sulfate ion concentrations since the calcium ion concentration is controlled by the solubility equilibrium of calcium sulfite. Thus, the scaling should depend on the rate of oxidation and on the pH of the solution. The rate of oxidation strongly depends on the pH of the solution. Above pH 7 and at high suspension concentrations, the suspensions were practically stable and little or no oxidation occurred. Even at pH 3, the oxidation of $CaSO_3$ suspensions proceeded slowly after a significant induction time.

Based on the presented evidence, we would like to draw the following tentative conclusions:

(1) Eliminating $CaSO_3$, $Ca(OH)_2$, and $CaCO_3$ as potential scale formers, scaling should occur only at high conversions at low pH values.

(2) The scaling is most probably the result of a sequence of processes: dissolution of calcium sulfite, oxidation in the dissolved state, precipitation of calcium sulfate with potential further conversion to anhydrite scale.

(3) The kinetics of each of these processes must be studied to identify the rate controlling step.

(4) There is sufficient evidence from desalination practice that even if the oxidation to sulfate cannot be prevented, scale-free operation can be achieved by proper selection of operating variables affecting the equilibria and kinetics of the process.

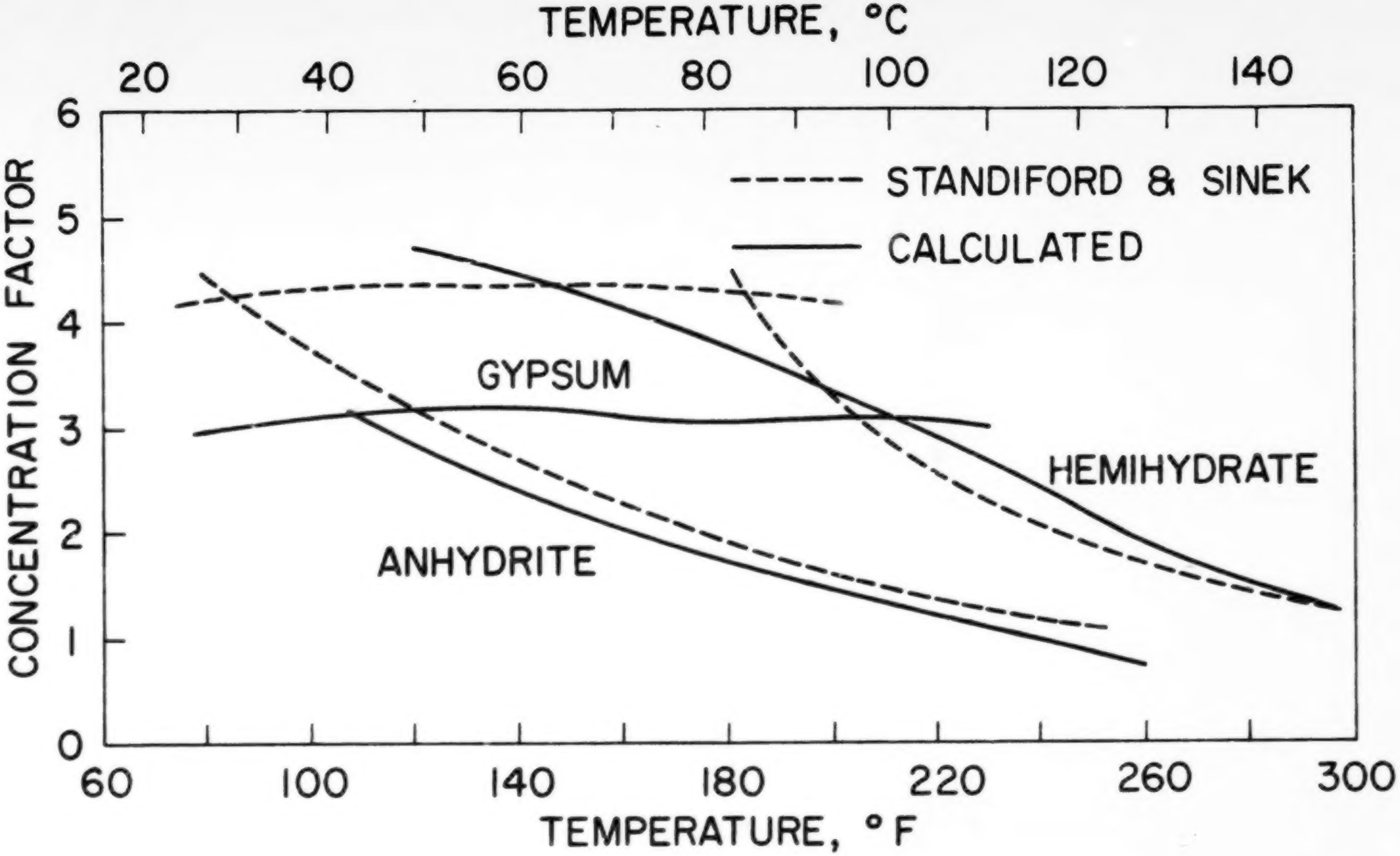

TEMPERATURE, °C
20
40
60
80
100
120
140
STANDIFORD & SINEK
CALCULATED
GYPSUM
HEMIHYDRATE
ANHYDRITE
CONCENTRATION FACTOR
6
5
4
3
2
1
0
60
100
140
180
220
260
300
TEMPERATURE, °F

FIGURE 1

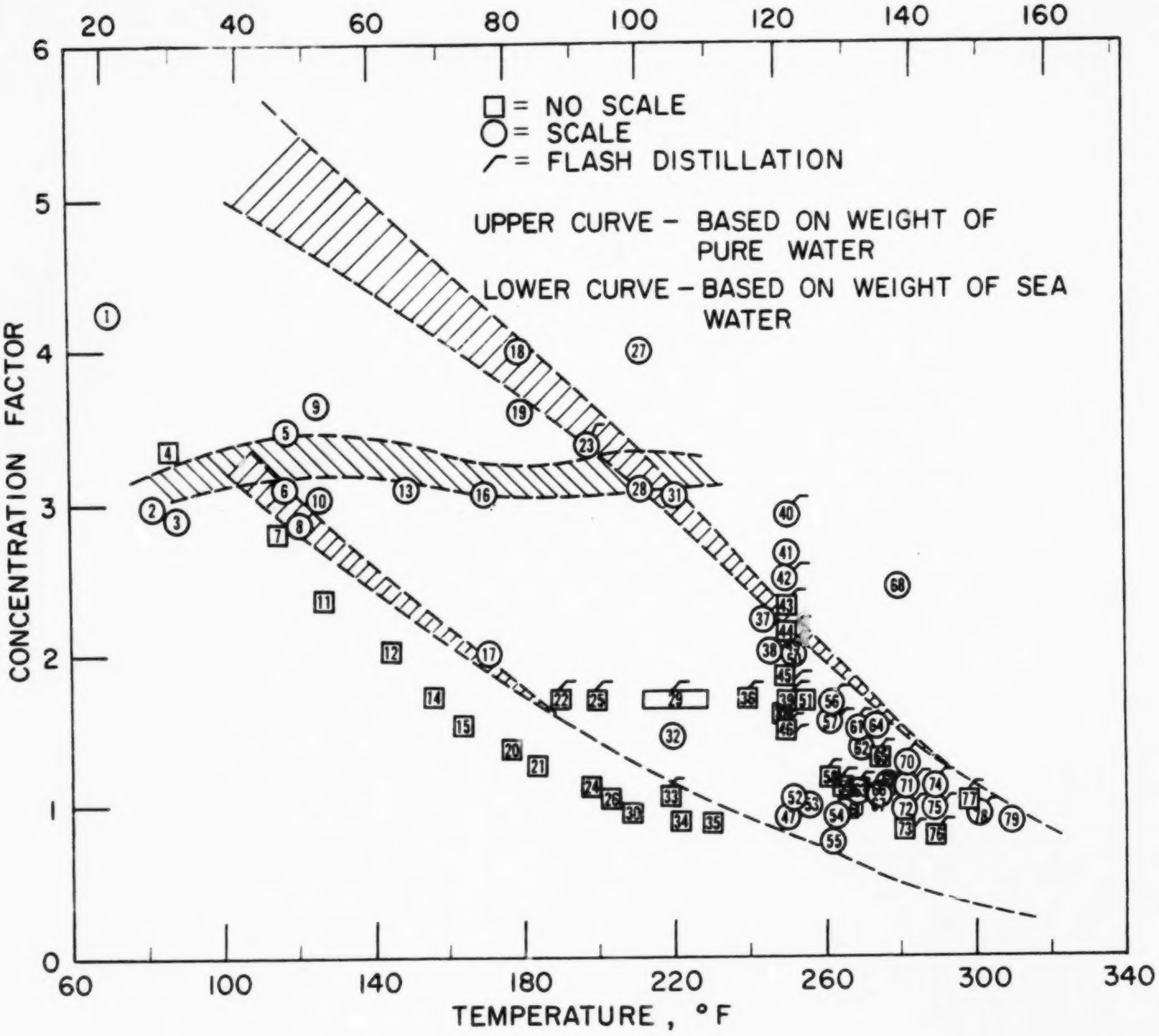

□ = NO SCALE
○ = SCALE
⌐ = FLASH DISTILLATION
UPPER CURVE - BASED ON WEIGHT OF PURE WATER
LOWER CURVE - BASED ON WEIGHT OF SEA WATER
CONCENTRATION FACTOR
0
1
2
3
4
5
6
TEMPERATURE , °F
60
100
140
180
220
260
300
340
20
40
60
80
100
120
140
160

FIGURE 2

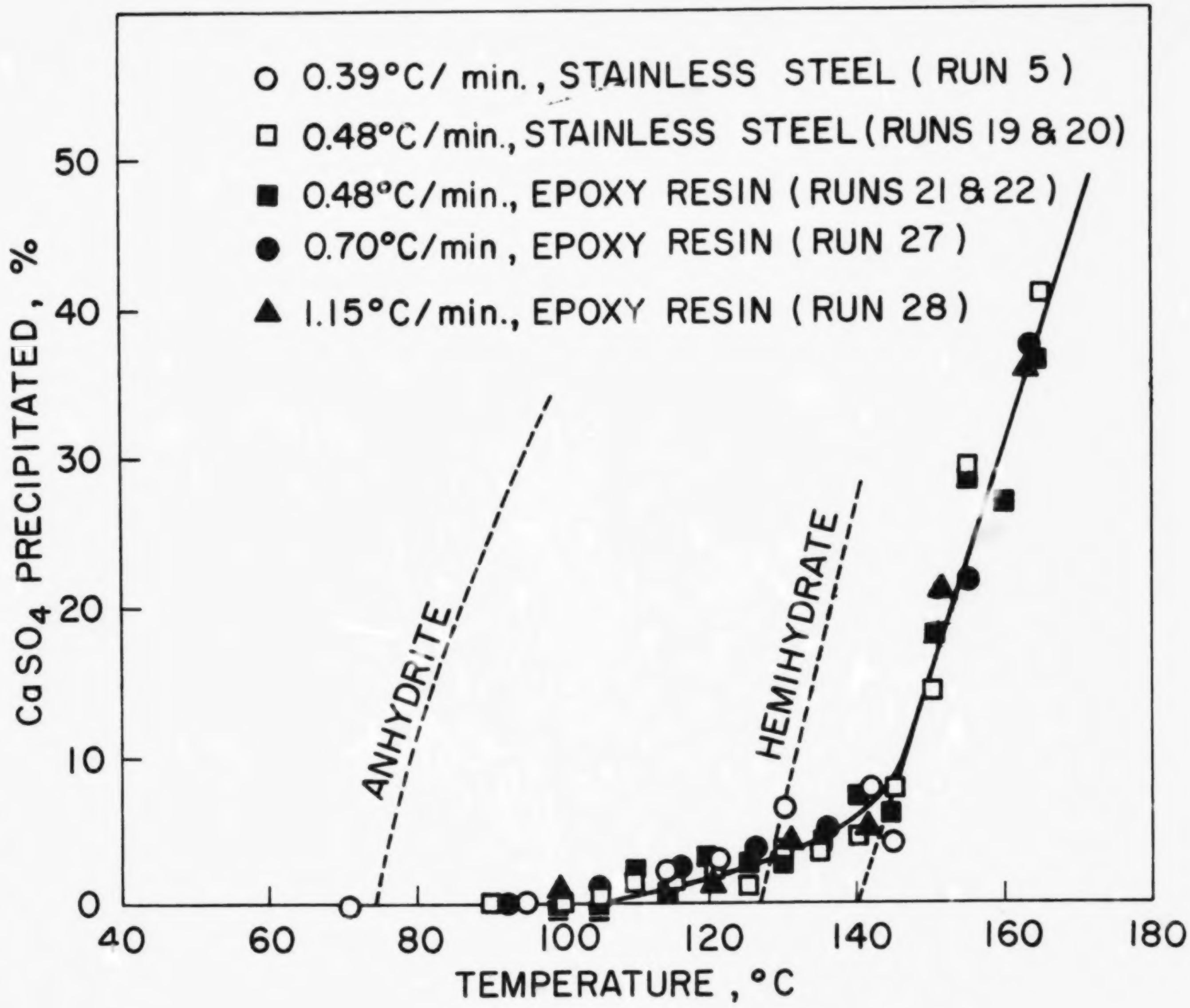

○ 0.39°C/ min., STAINLESS STEEL (RUN 5)
□ 0.48°C/min., STAINLESS STEEL (RUNS 19 & 20)
■ 0.48°C/min., EPOXY RESIN (RUNS 21 & 22)
● 0.70°C/min , EPOXY RESIN (RUN 27)
▲ 1.15°C/min., EPOXY RESIN (RUN 28)
ANHYDRITE
HEMIHYDRATE
$CaSO_4$ PRECIPITATED, %
0
10
20
30
40
50
40
60
80
100
120
140
160
180
TEMPERATURE , °C

FIGURE 3

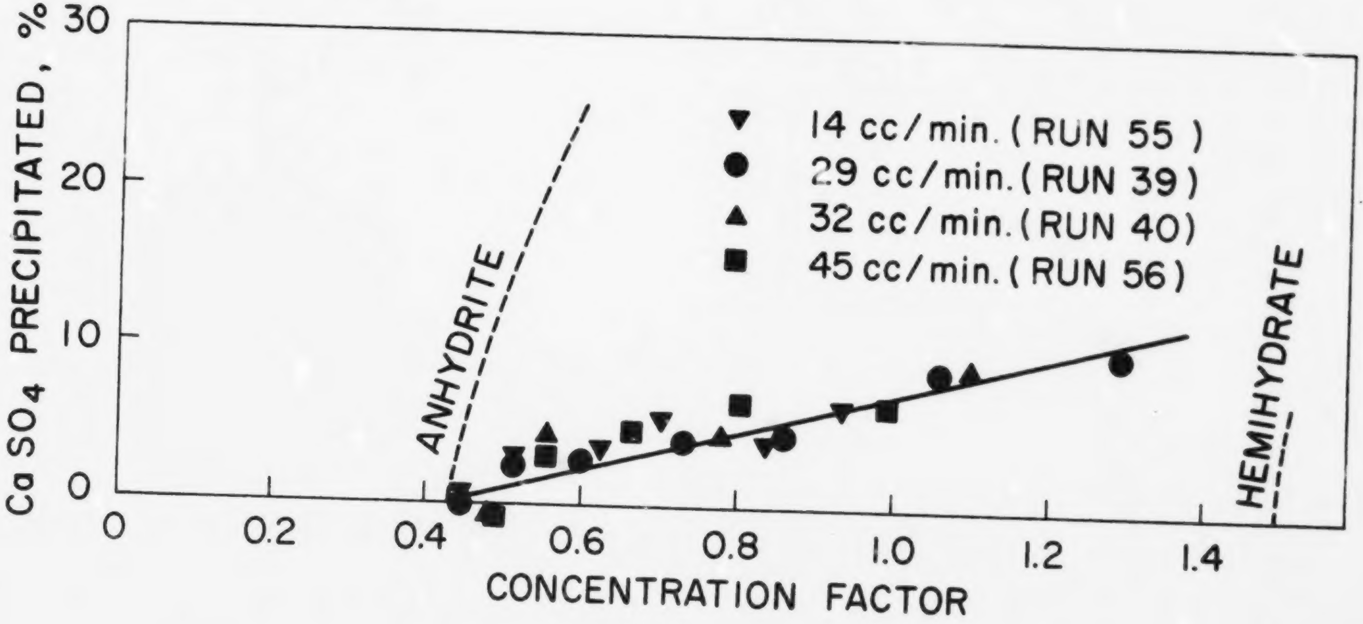

Ca SO4 PRECIPITATED, %
30
20
10
0
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
CONCENTRATION FACTOR
ANHYDRITE
HEMIHYDRATE
▼ 14 cc/min. (RUN 55)
● 29 cc/min. (RUN 39)
▲ 32 cc/min. (RUN 40)
■ 45 cc/min. (RUN 56)

FIGURE 4

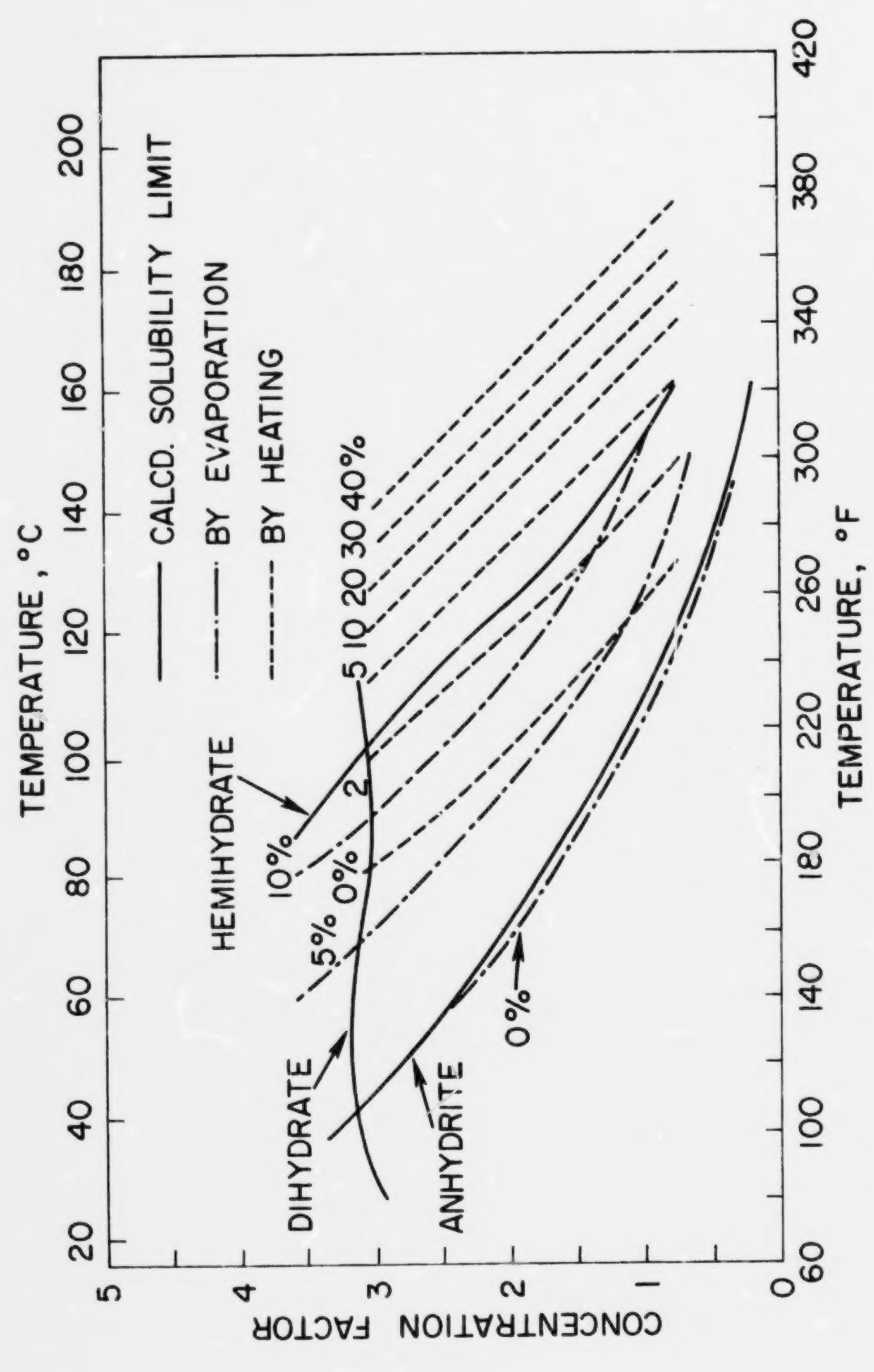
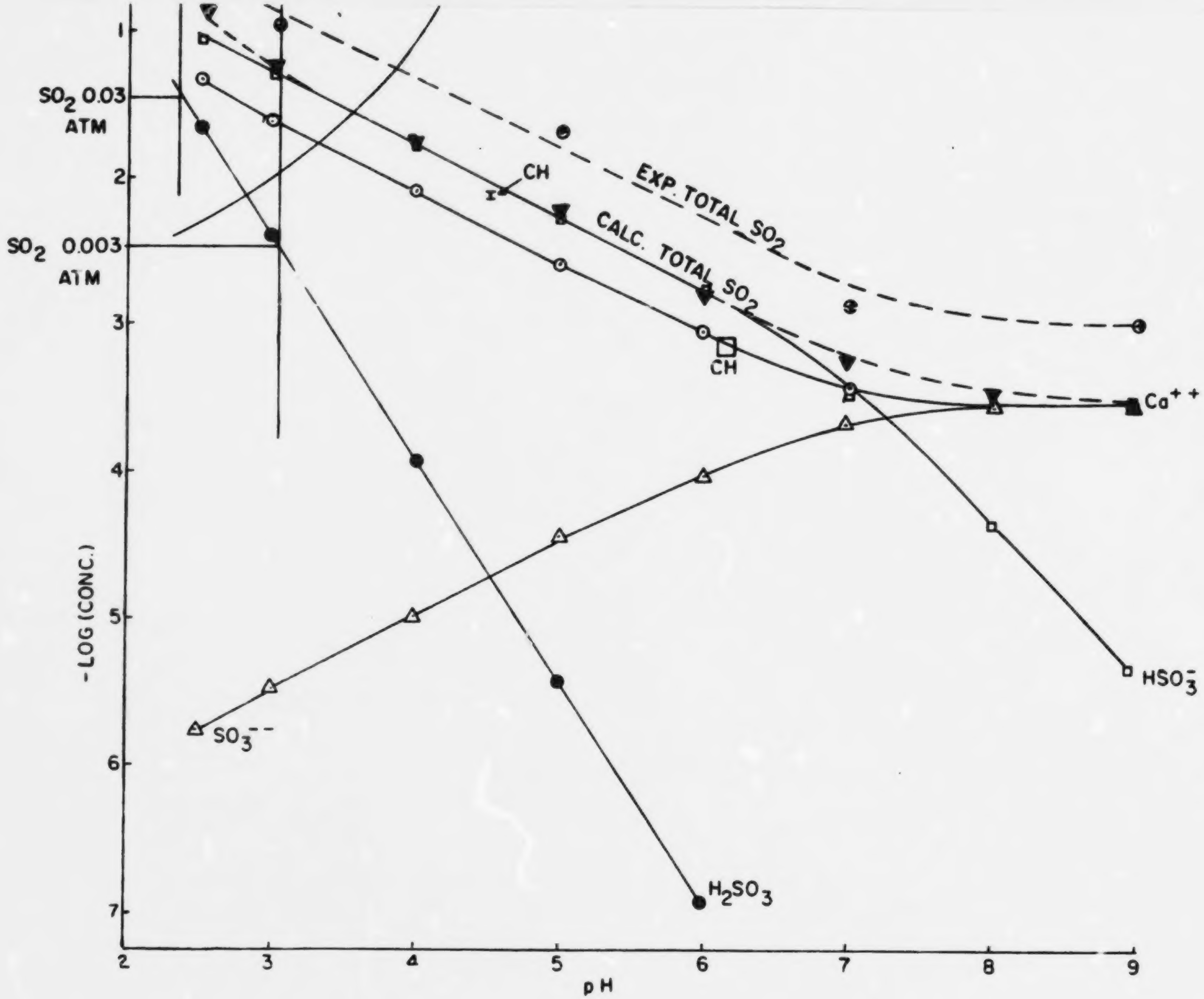

TEMPERATURE, °C
20
40
60
80
100
120
140
160
180
200
TEMPERATURE, °F
60
100
140
180
220
260
300
340
380
420
CONCENTRATION FACTOR
0
1
2
3
4
5
CALCD. SOLUBILITY LIMIT
BY EVAPORATION
BY HEATING
HEMIHYDRATE
DIHYDRATE
ANHYDRITE
10%
5%
0%
2
0%
5 10 20 30 40%

FIGURE 5



EQUILIBRIUM CONCENTRATIONS IN THE $CaO-SO_2-H_2O$ SYSTEM

REVIEW OF SCALING PROBLEMS IN LIMESTONE BASED WET SCRUBBING PROCESSES

By: Joan B. Berkowitz
Arthur D. Little, Inc.
Cambridge, Massachusetts

November 11, 1971

REVIEW OF SCALING PROBLEMS IN LIMESTONE BASED WET SCRUBBING PROCESSES

I. General Considerations

Scaling involves the precipitation of insoluble salts from aqueous solutions onto process equipment surfaces. Any salt may precipitate if its solubility limit is exceeded at some point in the processing stream. From the point of view of thermodynamics or equilibrium, solubility is a function of specific concentrations of the precipitating ions, total ion concentration, local temperature, and pH. Kinetically precipitation will not necessarily occur, even if the theoretical solubility limit is exceeded for a given salt, since some degree of supersaturation is typical of crystallization phenomena generally, and in many practical cases a very high degree of supersaturation can be sustained. Precipitation per se is not scaling. A precipitate becomes a scale when it attaches itself to a solid surface, either by nucleation and growth directly on the surface or by migration of particulates from the bulk of the solution to the walls. A precipitate which forms within the body of a solution can be carried in suspension within the processing stream and will not result in scale formation unless it is carried to the walls and tends to adhere there.

The salts most comonly found as components of scale are: $CaSO_4$ (anhydrite), $CaSO_4.2H_2O$ (gypsum); $CaSO_4.1/2\ H_2O$ (hemihydrate); $CaCO_3$; $CaSO_3.2H_2O$; and $Mg(OH)_2$. In fact, any wet process in which calcium or magnesium sulfites or sulfates must be handled is prone to scaling problems. For example, saline water distillation processes, wet phosporic acid manufacturing processes, as well as limestone/dolomite wet scrubbing processes for removal of sulfur dioxide have all been very much troubled by the deposition of scale on heat transfer and other surfaces. Accumulation of scale in pipelines, orifices, and other flow passages results in plugging of the equipment, often to the point where it becomes inoperable. In the wet phosphoric acid process, calcium sulfate formed by reaction between calcium phosphate ore and sulfuric acid, typically crystallizes in lines to the extent that periodic shutdown is necessary.

The so-called scale forming compounds listed above have two significant characteristics in common. First, the salts exhibit inverse solubility behavior; i.e., they become less soluble as solution temperature increases. Second, the salts tend to form relatively stable, supersaturated solutions. The inverse solubility as a function of temperature is probably the major factor responsible for ordinary boiler scale, and for the scaling of heat transfer surfaces in saline water evaporation plants. Scaling under relatively isothermal conditions may often be ascribed to uncontrolled precipitation from highly supersaturated solutions unto receptive surfaces of process equipment.

II. Wet Limestone Scrubbing Processes

A generalized wet limestone scrubbing process is schematically depicted in Figure 1 and represents several alternative methods of operating an SO_2 scrubbing process using calcium based reactants. As in the wet limestone/dolomite injection process developed by Combustion Engineering and Union Electric, the limestone can be calcined in the boiler and hydrolized as it is removed from the gas stream in the scrubber. Alternatively, as in the Howden-ICI process, lime or limestone can be added outside the scrubber loop, thereby allowing greater flexibility of scrubber pH and scaling control.

A. Scale Control in the Howden-ICI Process

The introduction of alkali outside of the scrubber loop is not in itself sufficient to prevent scaling. It does, however, permit the application of a number of simple scale control techniques. In one of the early wet scrubbers, which was set up in Fulham around 1935, a scale 2-3 inches thick was found on scrubber surfaces within 72 hours after start-up. The key to eliminating the problem lay in the understanding and control of supersaturation behavior in calcium sulfate and sulfite solutions, the primary products or "make" of the wet scrubbing process. It was recognized that calcium sulfite and calcium sulfate solutions exhibit an apparent stability under conditions of fairly high supersaturation. If the scrubbing liquor is never permitted to become anything more than slightly supersaturated, then sulfite and sulfate precipitation in the scrubber loop will be very slow. The slight supersaturation can then be destroyed by precipitation at preselected sites

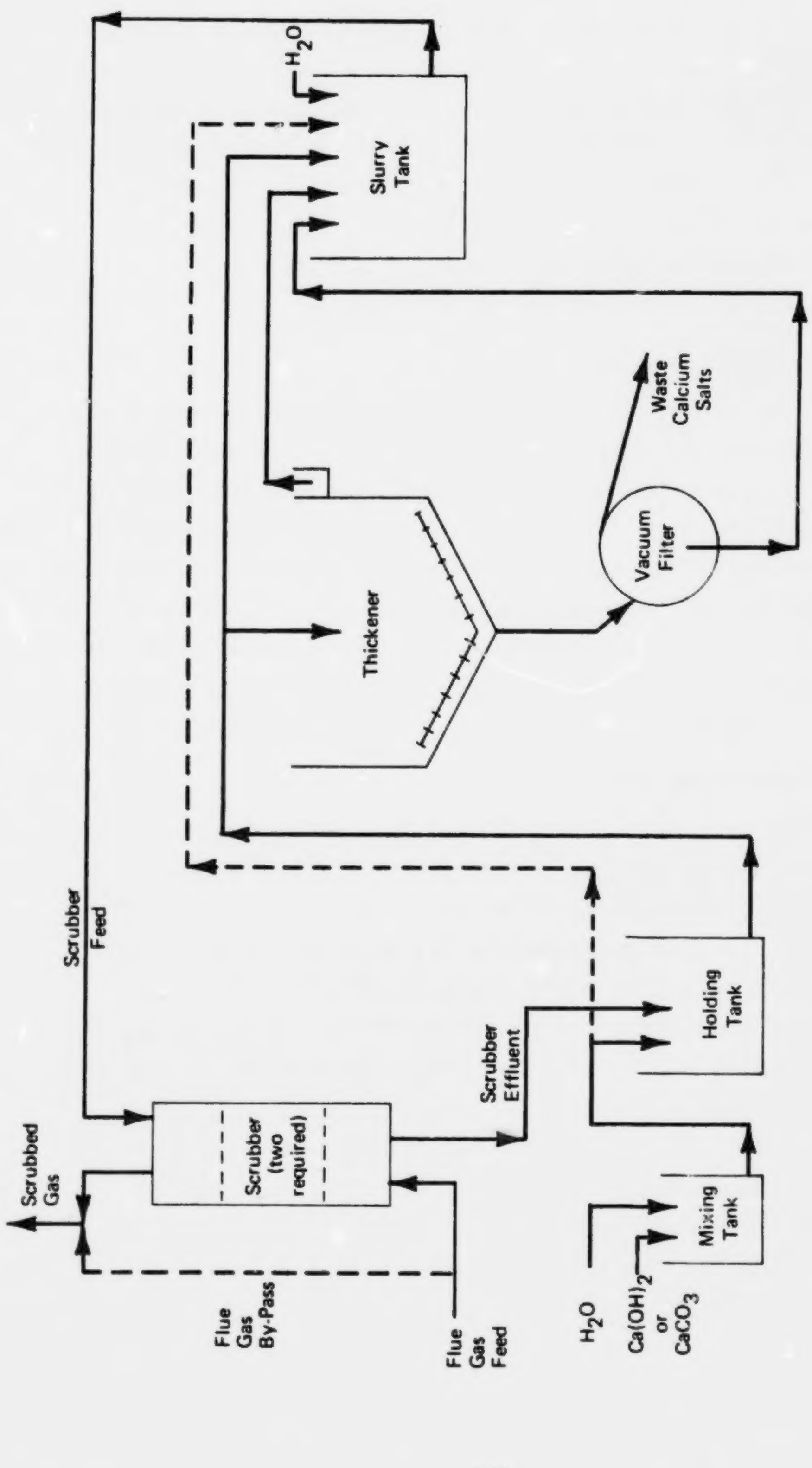


FIGURE 1 LIME OR LIMESTONE SLURRY SCRUBBING

so as not to interfere with normal scrubber operation.

The ICI group applied their understanding of supersaturation to effectively overcome scaling in their wet scrubbing operations. A three-pronged approach was used. First, the "make" of calcium sulfite and calcium sulfate per pass through the scrubber loop was controlled, by empirical adjustment of absolute flow rates and L/G ratios, so that the solutions formed were only slightly supersaturated. Second, a delay tank was introduced where supersaturation of the scrubbing liquor could be dissipated prior to recirculation. Third, suspended crystallites of calcium sulfite and sulfate, 3-5% of each, were carried in the circulating liquor to provide sites for homogeneous nucleation.

The above three measures taken to control supersaturation in the ICI wet scrubbing process went a long way towards alleviation of scaling problems. Other design factors, however, had to be taken into account before the problem could be completely eliminated. The solubility of calcium sulfite is decreased dramatically as pH is increased, even in the range 6 to 7. The pH must therefore be controlled so that the solubility change does not occur in the scrubbing tower where calcium sulfite might precipitate onto the packing. In the ICI process, the lime or limestone slurry is added just before the delay tank where the increase in pH assists in dissipating supersaturation. The rate of addition of alkali is adjusted so that the pH at the bottom of the scrubber is maintained at about 6.2. The total pH change through the scrubber is therefore from about 6.8 at the top to 6.2 at the bottom.

It has been implicit in the discussions so far that solutions and slurries are homogeneous in composition. It is naturally of prime importance that such uniformity in composition be maintained, at least to the extent that supersaturations are not exceeded in localized areas within the scrubbing tower. In the ICI work deep plates inserted in the lowest section of the scrubber tower provided for even gas distribution. The plates were also in a region of high sulfur loadings and the maintenance of high liquor velocities as well contributed to elimination of scaling in the system. It is interesting to note that in spite of the substantial progress made by ICI in the 1930's towards prevention of scaling by proper adjustment of design parameters, ICI was still troubled by occasional scaling problems when wet scrubbing operations were resumed in the 1950's. The problems were usually the result of incomplete irrigation of the scrubbing tower grids due to accidental blockage of flow elsewhere in the system.

Finally some materials and surface finishes are more resistant to nucleation, growth, and adherence of scale than others. In the ICI work, it was found that scaling could be minimized by constructing scrubber grids of smooth, planed red deal wood. The critical factors are probably corrosion resistance and surface smoothness.

B. Scaling in Limestone Injection Wet Scrubbing Processes

Although some of the ICI work involved the use of lime slurries, the bulk of the effort by far was concentrated on limestone additions. It is generally believed that lime is more efficient than limestone for removal of SO_2. However, the use of externally calcined lime adds substantially to the cost of scrubber operations. By introduction of limestone directly into the boiler, calcination of limestone may be accomplished very inexpensively. Unfortunately simultaneous introduction of lime and flue gas into the scrubber circuit has introduced scaling problems which are yet to be brought under control.

The key mechanism responsible for SO_2 absorption in limestone injection wet scrubbing process is believed to be the reaction of $SO_2(g)$ in the flue gas with a circulating saturated slurry of calcium sulfite, resulting in the formation of calcium bisulfite in solution:

$$CaSO_3 \text{ (sat. soln.)} + SO_2(g) + H_2)(1) \rightarrow Ca(HSO_3)_2 \text{ (soln)}$$

A sudden increase in pH in local areas, where hot lime particles from the boiler first contact the scrubber liquor, can force calcium sulfite out of solution with resultant plugging problems. The lack of pH control at the bottom of the scrubber may be a major factor contributing to scaling in limestone injection systems. Solution to the problem is not easy and might require major design changes.

In pilot plant experience with limestone injection wet scrubbing processes, scaling has been more the rule than the exception. In one installation which has been described in the literature, calcium sulfate deposited on overflow drain screens in the scrubber and drastically restricted water flow. Scaling and plugging were also encountered in the marble bed scrubber and in the reheater. The most serious scale problem was encountered at the scrubber inlet where temperature is at a maximum. It might be anticipated that this would be a critical position, due to the inverse temperature dependence of calcium sulfate solubility. Scaling at the scrubber inlet may be controllable through the use of saturated sprays to pre-cool the flue gas and to avoid the formation of a sharply defined wet/dry interface. This approach has been suggested by Bechtel, and is expected to be tested in the pilot plant later this year.

While the specific scale prevention methods devised by ICI for limestone slurry scrubbing are not all directly applicable to boiler calcined limestone injection scrubbing, the insights into the factors responsible for scale formation can provide guidance to the development of appropriate control techniques. The factors of primary importance are pH, both local and global; gas and liquor distributions; liquor velocities at scrubber surfaces; "make" of calcium sulfite and sulfate; scrubbing liquor composition; and materials of construction. Under EPA sponsorship, we are currently building a laboratory bench scale scrubber to explore the effect of these factors on scaling behavior.

III. Scale Composition

The principal components of the scale formed in the ICI limestone slurry process, before the scale control methods were optimized, were, gypsum ($CaSO_4.2H_2O$), 60-90%; $CaSO_3.1/2H_2O$, 1-40%; and calcite ($CaCO_3$), 1-5%. The ratio of sulfate to sulfite in the scale seems to depend on the degree of oxidation of sulfite in the scrubber circuit. This in turn seems to be highly sensitive to catalysis by trace quantities of transition metals.

Very little information seems to have been published about the composition of scales formed in the boiler calcined limestone injection processes. The absorption process is generally described in terms of sulfite-bisulfite reaction, but in the presence of fly-ash, oxidation of sulfite to sulfate is expected to be quite rapid. Since control of scale depends to some extent on composition and supersaturation behavior, the extent of sulfate formation could be an important and possible crucial process parameter. When a limestone slurry is used as a reactant, it is hardly surprizing that $CaCO_3$ might be a component of the scale. When limestone is calcined in the boiler prior to introduction to the scrubber, the calcining process is complete and virtually no $CaCO_3(s)$ is carried in the flue gas mixture. Any $CaCO_3$ found in the scale would thus have to be due to the reaction of CO_2 with scrubber liquor components. The role of CO_2 in the injection scrubbing process is very much in need of clarification. The critical step in the ICI process is supposed to be the reaction of $CaCO_3$ with CO_2 in the flue gas to form the bicarbonate which subsequently reacts rapidly with SO_2 to form sulfite. In the injection process, the absorption mechanism seems to involve primarily sulfite/bisulfite rather than carbonate/bicarbonate. If there is a real difference in mechanism, a different approach to control may be required.

DEPOSITION PROBLEMS AND SOLUTIONS IN THE COMBUSTION ENGINEERING LIME/LIMESTONE WET SCRUBBING SYSTEMS

J.R. Martin
Combustion Engineering, Inc.

Prepared for
Second International Lime/Limestone
Wet Scrubbing Symposium
New Orleans, Louisiana
November 8-12, 1971

Lime/Limestone Wet Scrubbing Symposium
Thursday, November 11, 1971
Session on Scaling Problems

J. R. Martin
Combustion Engineering, Inc.

It would appear that Combustion Engineering has been asked to participate in this session on scaling problems in lime/limestone wet scrubbing because of our vast experience in producing scale. The deposition problems which we have experienced in the C-E - APCS fall into two general categories. The first area includes all those deposits which are mechanical in nature (i.e., deposition of solids due to drop out at low gas velocities). The second area is limited to scale formation as a result of chemical reaction. My initial remarks will be related to the first type of deposition: mechanical.

Mechanical Deposition

The system schematic shown in Figure I of the C-E - APCS (limestone-furnace injection) at Kansas Power and Light Company, Unit #4 will serve as the reference for this discussion. The C-E APCS at Union Electric, Meramec Station is similar except for employing a clarifier rather than a pond; therefore, the statements herein are considered to be applicable to both systems.

The first deposition problem that was encountered was the mechanical plugging of the scrubber inlet. The inlet became 40-50 percent plugged within 24 hours of operation of the system. Figures II and III show the scrubber inlet plugged and clean. The clean inlet is as a result of installing a sootblower which prevents excessive build-up of deposits. This deposition is caused by the wet-dry interface at the scrubber inlet. The inlet deposit is typically composed of flyash, calcium sulfate, and calcium oxide bound together in a cementitious mixture. The calcium sulfate which has been found in the inlet deposit does not exhibit the crystalline type properties of calcium sulfate scale. It is our conclusion that the calcium sulfate found in the inlet deposit is a result of the removal of sulfur trioxide in the boiler by the injected limestone; this is verified by the fact that the composition of the inlet deposits are quite similar to that of the dust entering the APCS.

Another area of mechanical deposition is the area under the marble bed. This area includes the underbed spray system, the marble bed structural supports, the gas straightening vanes, and the scrubber walls. Most of this deposition is also a result of wet-dry interfaces. The flue gas entering the scrubber is 300-350°F and is cooled down to its saturation temperature (110-128°F) in the area under the marble bed. During this cooling, some of the hot dry flue gas impinges on partially wetted surfaces and deposition of the dust being carried by the flue gas can result.

The reheater and demister (shown in Figure I) are two components of the APCS with which we have experienced deposition and scaling problems. The deposition of mud (chemically uncombined solids) on the demister occurs in normal operation of the system to a minor extent. This build-up of solids is cleaned by the utilization of a demister wash system, but when the marble bed is not operating correctly, excessive build-up of solids can occur which the wash system cannot cope with. Additionally, calcium sulfate scale is formed in the demister when the scrubber becomes supersaturated with calcium sulfate. The liquid which the demister is separating has the highest concentration of calcium sulfate in the scrubber and therefore, the greatest tendency to scale is at this point. The problem of supersaturation of calcium sulfate and the resulting scaling will be discussed in subsequent remarks. Also the APCS reheater builds up calcium sulfate scale when the demister is not operating properly. The excess liquid impinging on the reheater is evaporated leaving anhydrous calcium sulfate. This deposit is very hard even withstanding sand blasting.

Chemical Scale

Basically, we have formed three types of chemical scale in the C-E - APCS limestone scrubbing process: calcium carbonate, calcium sulfate, and calcium sulfite. These three types of scale have been found in many locations throughout the APCS. My remarks on this subject will be limited to where we have formed these different scales, what we think the mechanism or reaction is that causes them to form, and how we have eliminated or minimized their formation.

The marble bed is where we have experienced our most severe scaling problems. Scaling of both calcium sulfate and calcium sulfite has occurred on the overflow pots, recycle piping, and in the marble bed.

Calcium Sulfate

Figure IV is the marble bed at Meramec Station, Union Electric Company APCS, after about 24 hours of operation in the fall of 1968. The deposition on the overflow pots is a mixture of calcium sulfate scale and flyash. The flyash appears to get trapped in the deposit as the calcium sulfate is scaling. The deposit has a definite crystalline shape and reflects light similar to chips of glass. The calcium sulfate scale also was found on the scrubber walls.

This problem of calcium sulfate scale was not encountered in our earlier pilot plant work and was therefore unexpected. Initially, we thought the scaling might be due to the retrograde solubility that calcium sulfate exhibits (i.e., liquid temperature in the scrubber is higher than the liquid temperature in the clarifier). This theory was weakened when it was determined that the form of calcium sulfate we were scaling was gypsum and not anhydrous. There is no change in gypsum's solubility in the temperature range that the C-E - APCS operates.

Next, we switched to the use of a dolomitic limestone and the higher magnesium seemed to depress the overall calcium in solution to a point where it did not scale calcium sulfate. In the late fall of 1969, the calcium sulfate scaling problem occurred again. This occurrence was probably due to longer sustained periods of operation of the APCS. It was at this time that we added some additional dilution water to the system in order to maintain the calcium sulfate concentration below the scaling level. The rate of dilution water we determined that was required to run Meramec was equivalent to about two gallons per thousand acfm. We are not suggesting that this is the best way to prevent sulfate scaling, but at that time it alleviated the problem and enabled further operation of the system.

To date, we have never seen sulfate scaling in the scrubber at Kansas Power and Light, Lawrence No. 4. Tests this year in our laboratory suggest that the pond in Kansas (we go directly from the scrubber to the pond) acts as a desaturating vessel, in other words, the scrubber effluent which is supersaturated in calcium sulfate solution going to the pond will be reduced to saturation given sufficient time. In fact, the calcium sulfate concentration in the spray water from the pond has never gone higher than 1200 ppm. Whether this is due to the action of the pond or that we have not operated for a long enough period of time to completely saturate the pond is not known.

Calcium Sulfite

The sulfite scaling problem we encountered occurred when we tried to recycle the solids from the bottom of the scrubber to above the bed. Figure V shows a recycle nozzle at Kansas Power and Light; the spray pattern of this nozzle is a hollow cone; it looks like an inverted umbrella. All the deposit on the bottom of the nozzle is pure calcium sulfite. We have explained the formation of this type of scale as follows: there is a localized area highly concentrated in calcium hydroxide where the recycle slurry enters the bed. This highly alkaline slurry raises the pH of the bed liquid causing a shift in the bisulfite-sulfite equilibrium. Scaling of calcium sulfite results because of its relatively low solubility. Later, when we installed a system where part of the pot effluent water was pumped to the recycle tank and controlled the recycle slurry pH, we found that we could operate the recycle system without sulfite scale.

Figure VI shows another view of the same marble bed. The diagonal white line down the middle of the figure is where the division plate is located under the marble bed; it is a localized area of low gas velocity which readily plugs during normal operation. The other light areas are the type of deposit which results when the recycle slurry pH is not controlled.

Figure VII shows the marble bed at K. P. & L., Lawrence No. 4 after we revised our recycle system and rearranged the overflow pots. We have been able to run for a two-and-one-half week period last June with this revised above-bed recycle system without any sulfite scale formation in the scrubber system.

Calcium Carbonate

The other type of scaling problem we have experienced is calcium carbonate scaling. In January of 1971 we incurred severe scaling of calcium carbonate at Kansas Power and Light Company. We were trying to run some tests on the system to determine the effect of recycle at the time. One particular series of tests required running the system without recycle. During this test very high limestone feedrates to the furnace were required to obtain reasonable sulfur dioxide removal. Since there was no recycle of the scrubber reject slurry, the scrubber effluent slurry to the pond rose to a pH of 10. Gradually, the pond pH started rising and when it rose to 10, we developed a serious problem of calcium carbonate scaling in the spray nozzles of both scrubbers.

The scrubber effluent comes in at the left of the pond (Figure VIII is a picture of the pond) and then the liquid travels around the pond to the spray water pumps. The pond is simultaneously used for the plant's cooling tower blowdown, their bottom ash blowdown, and their pyrites blowdown. At the time that the $CaCO_3$ scaling problem occurred, the cooling tower blowdown was coming into the pond at the APCS spray water pump suction. The cooling tower blowdown had been pumped into this area of the pond since the system was started up in 1968 without any problems.

The cooling tower blowdown water has about 400 ppm of bicarbonate. Further, the quantity of cooling tower blowdown water entering the pond is roughly equivalent to 1500 gpm whereas the spray water to the APCS is 3600 gpm. It has been theorized that the pH rise which occurred in the pond last January caused a shift in the bicarbonate-carbonate equilibrium and since calcium carbonate is a very insoluble compound it became saturated and subsequently scaled in the spray piping system as it left the pond. Naturally, the first place where the problem would become serious would be in the orifice of the spray nozzle.

After analyzing the problem, we moved the location where the cooling tower blowdown enters the pond to the same place where the scrubber effluent slurry enters the pond. In this way the pH rise which may or may not occur depending on the APCS mode of operation will take place on the inlet side of the pond, thereby allowing the bicarbonate-carbonate shift and the resulting precipitation of the calcium carbonate to have sufficient time to take place in the pond rather than the scrubber. Subsequent operation of the system has not produced any calcium carbonate scale.

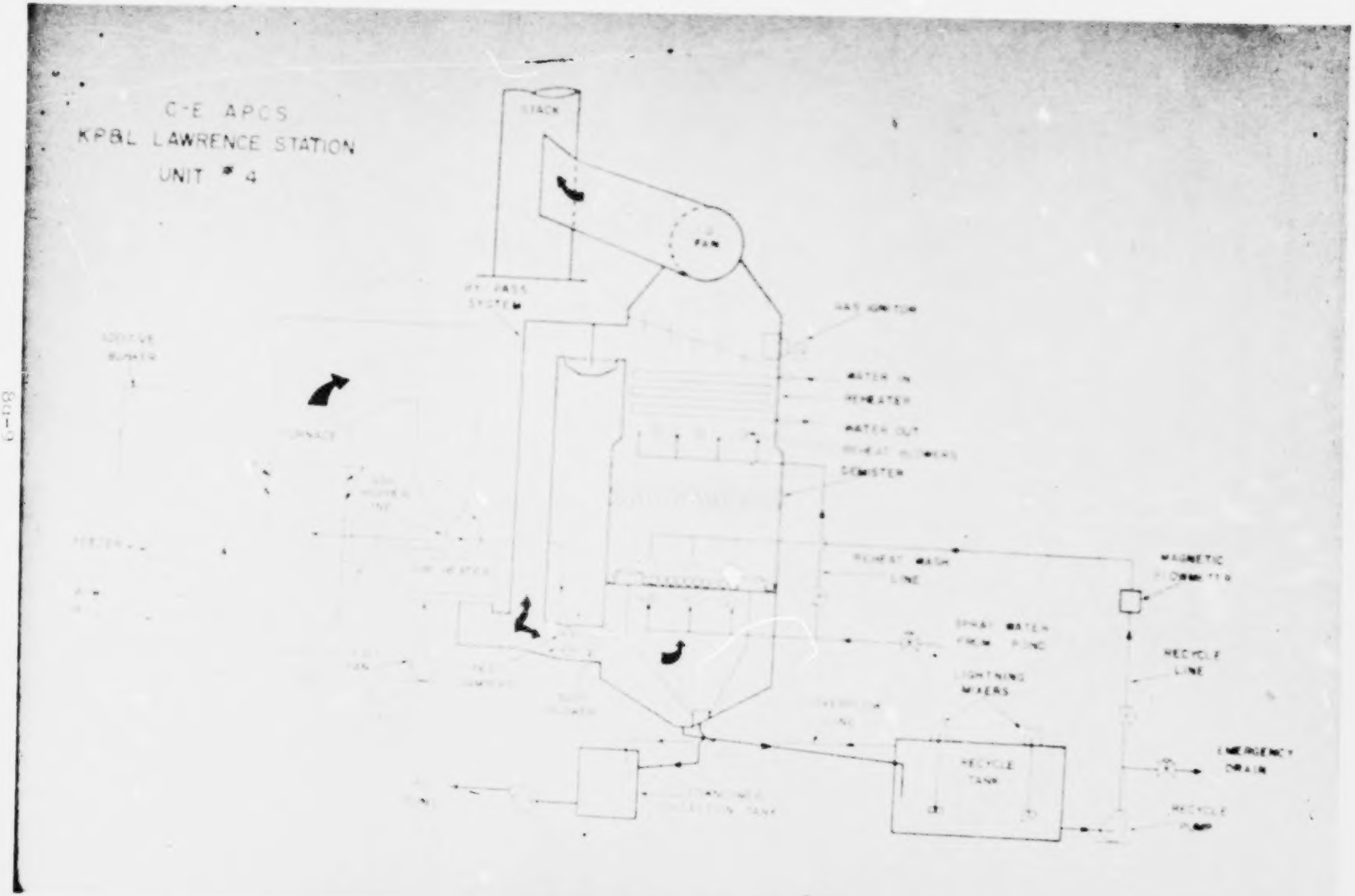

C-E APCS
KPBL LAWRENCE STATION
UNIT # 4
STACK
FAN
BY-PASS SYSTEM
ADDITIVE BUNKER
FURNACE
AIR HEATER
GAS IGNITOR
WATER IN
REHEATER
WATER OUT
REHEAT BLOWERS
DEMISTER
REHEAT WASH LINE
MAGNETIC FLOWMETER
SPRAY WATER FROM POND
RECYCLE LINE
LIGHTNING MIXERS
RECYCLE TANK
EMERGENCY DRAIN
RECYCLE PUMP
COLLECTION TANK

Figure I

Figure 11

Figure III

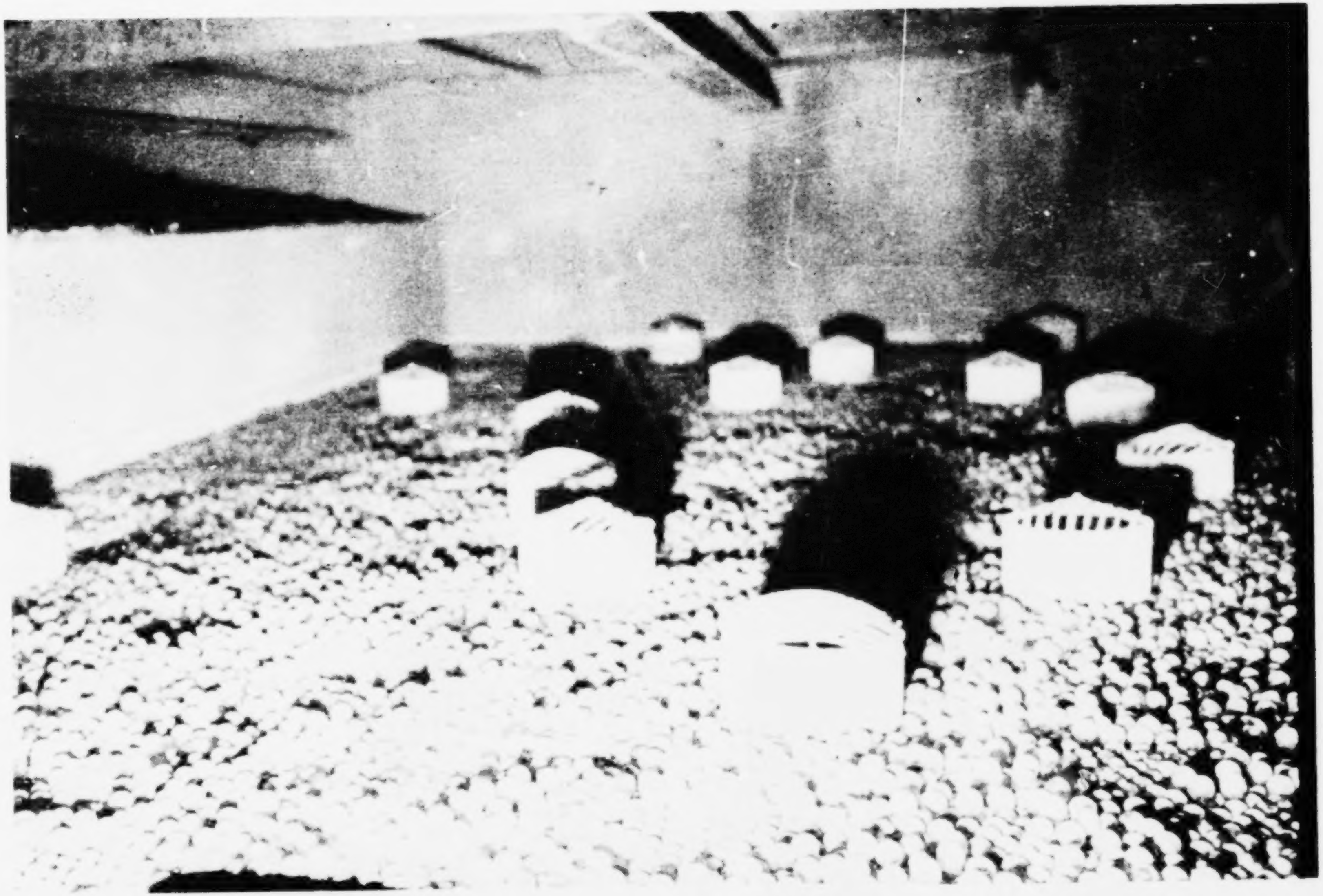


Figure IV

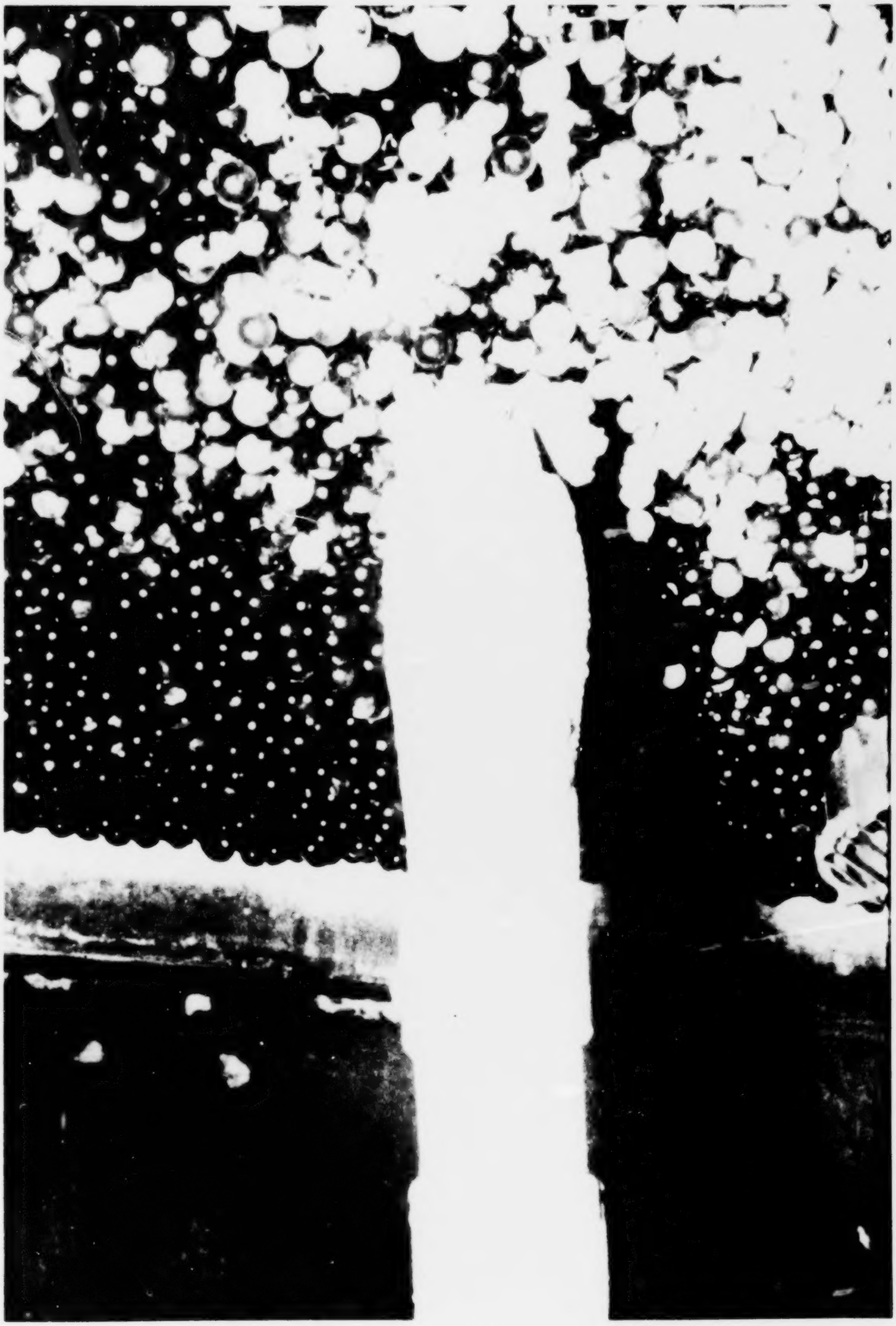


Figure V

Figure VI

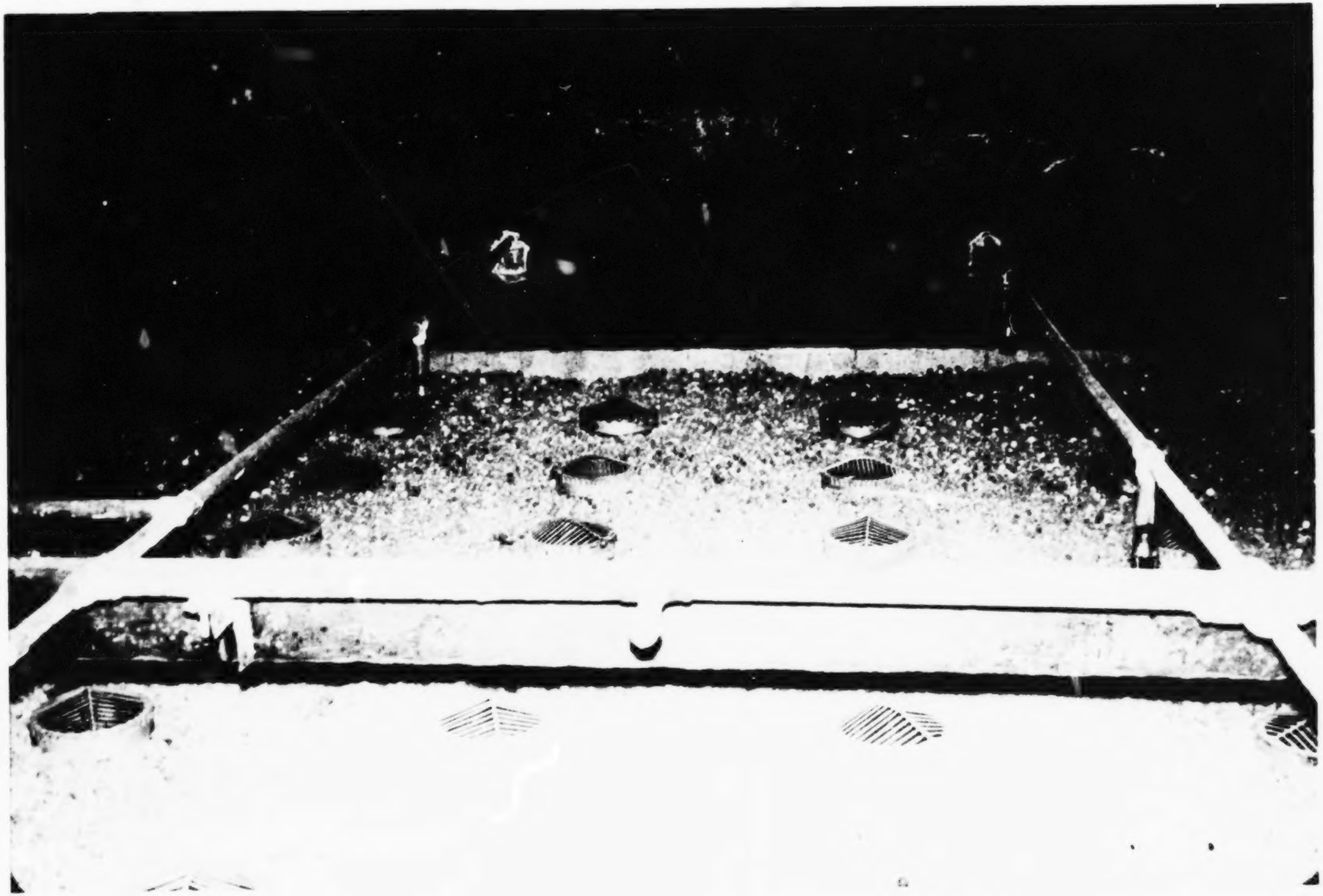


Figure VII

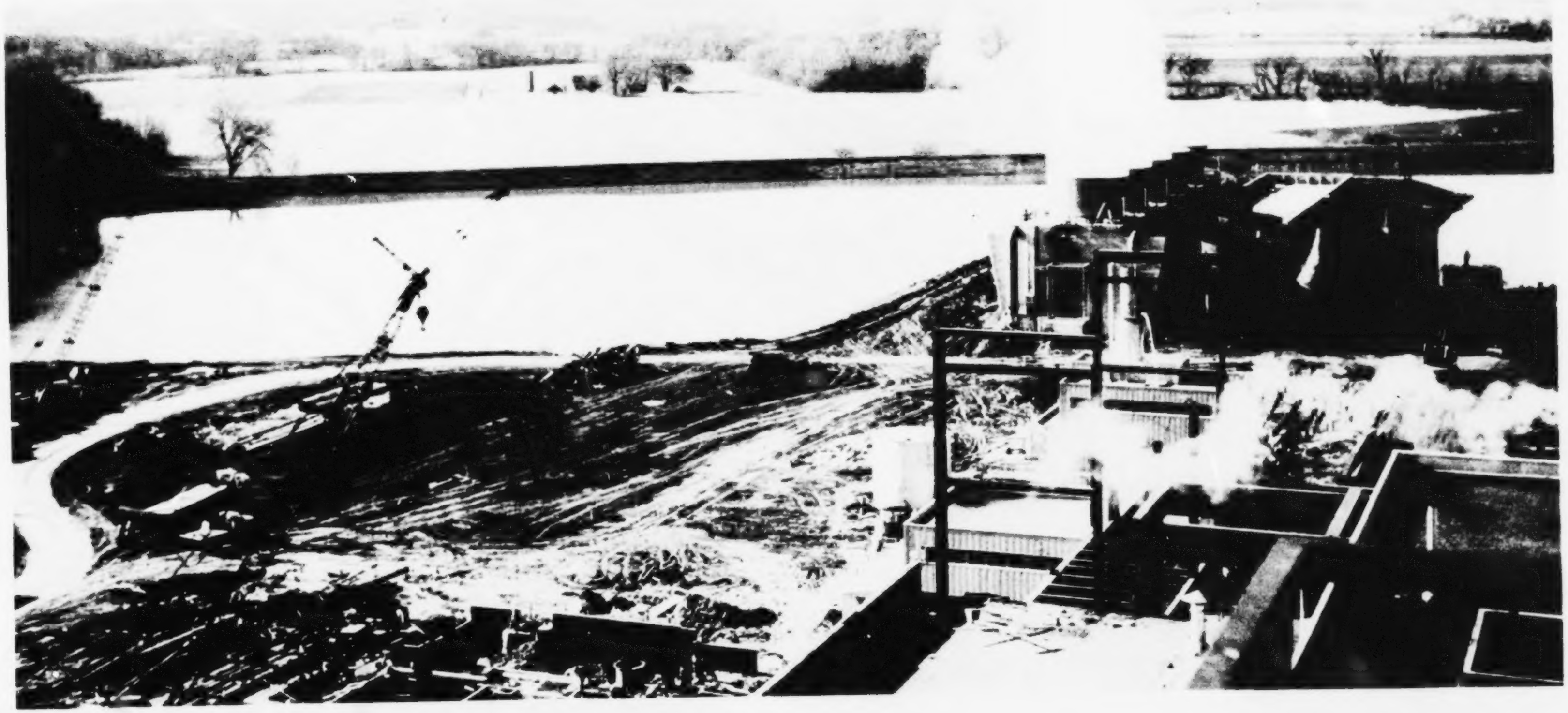


Figure VIII

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USE OF CHEMICAL ANALYSIS AND SOLUTION EQUILIBRIA IN PREDICTING CALCIUM SULFATE/SULFITE SCALING POTENTIAL

by:

Philip S. Lowell

Presented at:

SECOND INTERNATIONAL LIME/LIMESTONE
WET SCRUBBING SYMPOSIUM
8-12 November 1971
Sheraton-Charles Hotel
New Orleans, Louisiana

Sponsored by:

Environmental Protection Agency
Office of Air Programs
Division of Control Systems

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1.0 INTRODUCTION

This paper presents experimental data from a TVA pilot plant. These data are consistent with a proposed quantitative measure of scaling potential. Both calcium sulfate and calcium sulfite precipitation could be anticipated in the system studied. The possibility of scale formation in the scrubber or on vessel walls existed for both sulfate and sulfite, while sulfite scaling could also take place on limestone feed crystals, a phenomenon known as "blinding".

The principle object of understanding scaling phenomena is to be able to design and operate a process that does not scale. This requires that three types of information be known:

- A description of the individual major pieces of equipment used in the process including kinetic data, equilibrium conditions, and mass and heat balances.
- A description of the entire system.
- The ability to predict in quantitative, measurable terms the scaling potential in all the different parts of the system.

The equipment descriptions for particular types of scrubbers have been discussed in Papers 1a and 1b and the first two requirements have been treated in general by Dr. Ottmers in Paper 1c.

The third requirement for design of a scale-free process, a quantitative measure of scaling potential will be discussed in more detail in Section 2.0. The proposed method, which was first presented by Mr. J. L. Phillips in Paper 1d involves some function of the relative supersaturation, i.e., the quotient of activity product and solubility product constant.

The experimental results presented here were obtained at the Tennessee Valley Authority's Colbert Steam Plant. A pilot plant is being operated there in support of a full-scale plant to be designed for the Widow's Creek facility. The objectives of the Colbert pilot operation are to obtain design and operating data and to find out whether the scrubber and ancillary vessels can be operated without scale formation. The results during an extended period of operation at relatively constant conditions showed that no scaling occurred. Radian collected data in the middle of this period.

2.0 A QUANTITATIVE MEASURE OF SCALING POTENTIAL

In this section, the basis for the proposed scaling potential function will be discussed and some basic laboratory results will be referred to. Although laboratory studies have been conducted only for calcium sulfate dihydrate precipitation, it is expected that the same kind of behavior will be shown for calcium sulfite in future work. While anhydrous calcium sulfate is the thermodynamically stable form above 40°C, the formation kinetics are much too slow for it to be of significance in any system.

The use of concentration terms (molalities or molarities) in place of activities does not give a good description of behavior in a system of high ionic strengths. Equations 2-1 and 2-2 relate activity, molality and ionic strength, and Figure 2-1 shows the normal type of relationship between activity coefficient and ionic strength.

$$a_i = \gamma_i m_i \qquad (2\text{-}1)$$

$$I = \tfrac{1}{2}\Sigma\, m_i z_i \qquad (2\text{-}2)$$

In solutions of high ionic strength such as those encountered in limestone scrubbing, activities differ greatly from molalities. Therefore, measured chemical compositions must be used to calculate activities using equilibrium constants and mass balance equations. As an example, the amount of calcium found in solution by chemical analysis cannot be set equal to the molality or activity of the Ca^{++} ion.

The product of the activities of two ions is a measure of supersaturation or subsaturation with respect to the solid compound they can form by precipitation. At equilibrium, the activity product is equal to the solubility product constant, K_{sp}, and the solution is saturated. When the activity product is numerically greater than the solubility product constant, the solution is subsaturated, and there is a tendency for more of the compound to dissolve. These ideas are shown in Equations 2-3, 2-4, and 2-5 for calcium sulfate.

Equilibrium $$a_{Ca^{++}} a_{SO_4^=} = K_{sp_{CaSO_4}} \qquad (2\text{-}3)$$

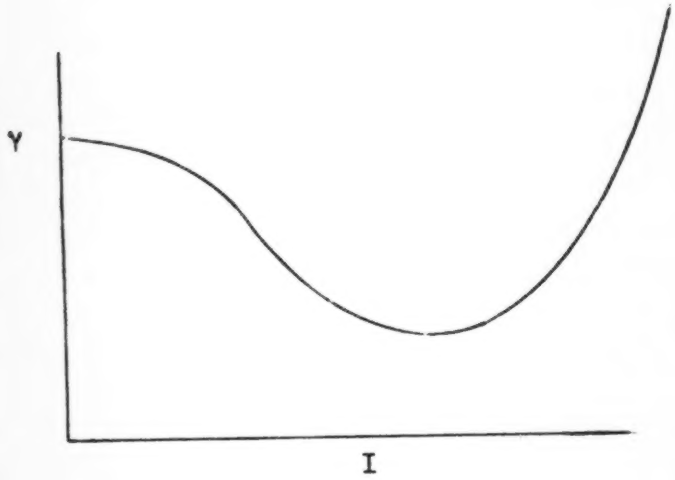

FIGURE 2-1

RELATIONSHIP BETWEEN ACTIVITY COEFFICIENT AND IONIC STRENGTH

Subsaturation: (dissolution tendency) $a_{Ca^{++}} a_{SO_4^=} < K_{sp_{CaSO_4}}$ (2-4)

Supersaturation: (precipitation tendency) $a_{Ca^{++}} a_{SO_4^=} > K_{sp_{CaSO_4}}$ (2-5)

Since the magnitude of K_{sp} varies widely for different compounds, it is convenient to "normalize" the means of expressing the degree of saturation by using the quotient $a_1 a_2/K_{sp}$. Then the relationships in 2-6, 2-7 and 2-8 are true for any compound formed from cation 1 and anion 2.

Equilibrium: $\frac{a_1 a_2}{K_{sp}} = 1$ (2-6)

Subsaturation: (dissolution tendency) $\frac{a_1 a_2}{K_{sp}} < 1$ (2-7)

Supersaturation: $\frac{a_1 a_2}{K_{sp}} > 1$ (2-8)

The quotient $a_1 a_2/K_{sp}$ has been termed the relative supersaturation, r. It is proposed that some function of the relative supersaturation is a valid and useful quantitative description of the tendency towards scale formation.

The phenomena of scaling and nucleation are somewhat related. Precipitation on an existing crystal requires only that the relative supersaturation be greater than one. Very small crystals are more soluble than large crystals. There is, therefore, some value of r greater than one that must be attained in the solution before a nuclei can be formed.

Scaling is somewhat similar to nucleation in that a new species is being formed. If the electrostatic forces and lattice spacing of the host surface is very close to that of the scaling species a value of r close to one might be sufficient to cause scale nuclei. If the host surface is very dissimilar the value of r will probably be near that required for bulk nucleation. While this is perhaps a rather folksey description of a complex phenomenon, it does appear to have merit in correlating the results. The important point being made is that value of r required for nucleation should have some relationship to scaling.

Results obtained by J. L. Phillips in the Radian laboratory (Paper 1d) show clearly that for calcium sulfate there is indeed a critical value of relative supersaturation beyond which nucleation and a greatly increased rate of precipitation takes place. The results are illustrated in Figure 2-2 which shows that beyond a value of $a_{Ca^{++}}a_{SO_4^=}/K_{sp}$ of 1.3 to 1.4 the rate of calcium sulfate dihydrate precipitation markedly increases. Photographs of the crystals formed at values of the ratio greater than this critical value clearly indicate the formation of small new crystals where nucleation has occurred. Again, the data for calcium sulfite precipitation have not yet been obtained. However, the same behavior is anticipated for the sulfite.

3.0 EXPERIMENTAL CONFIRMATION

The equipment and flow arrangements for the pilot plant scaling studies are given in Figure 3-1. Again it should be pointed out that scale formation was not a problem in the system shown. This can be explained by examining the values of relative supersaturation for calcium sulfate and calcium sulfite throughout the system. For similicity, let r_1 be the relative

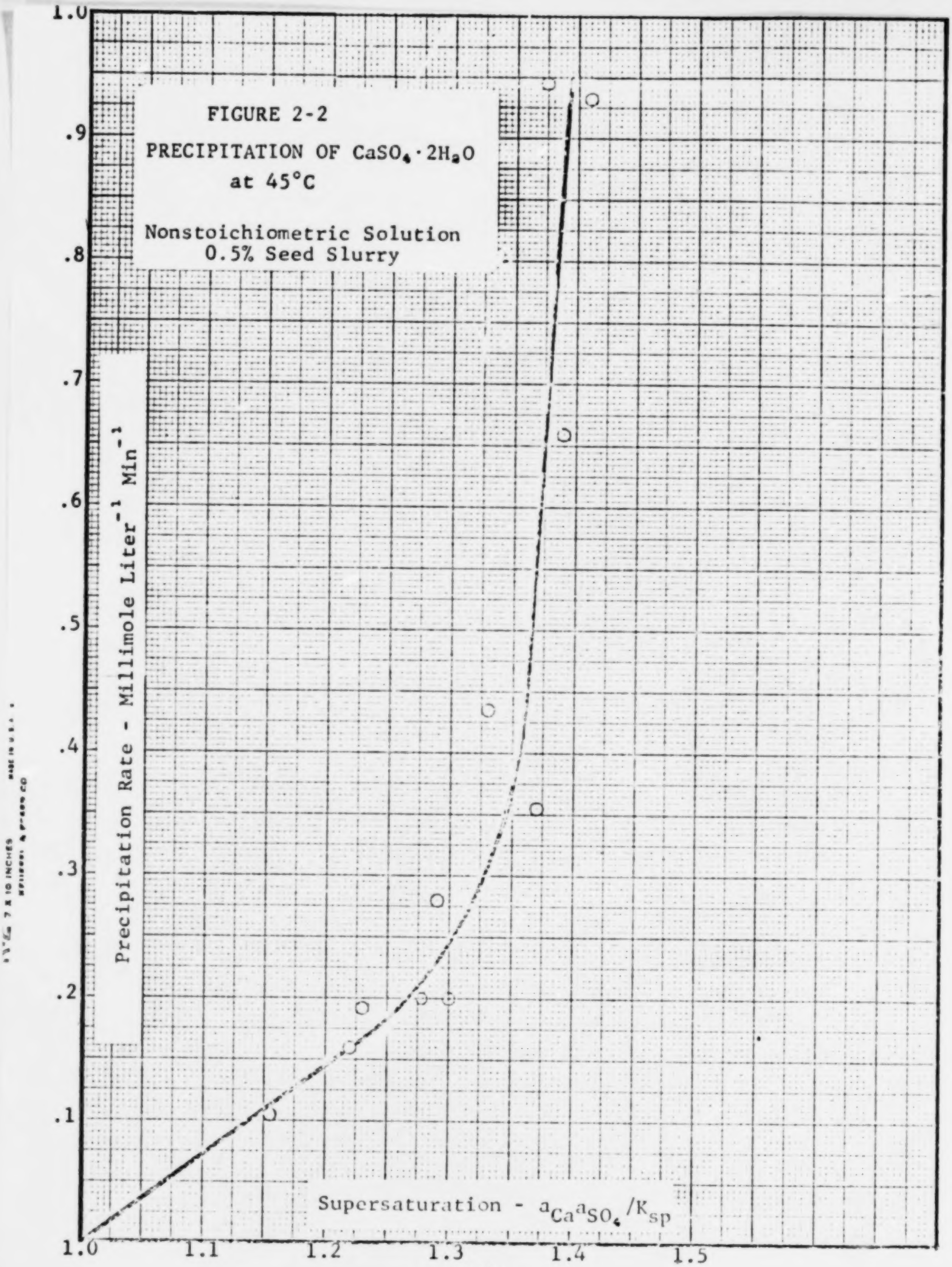

FIGURE 2-2

PRECIPITATION OF $CaSO_4 \cdot 2H_2O$ at 45°C

Nonstoichiometric Solution
0.5% Seed Slurry

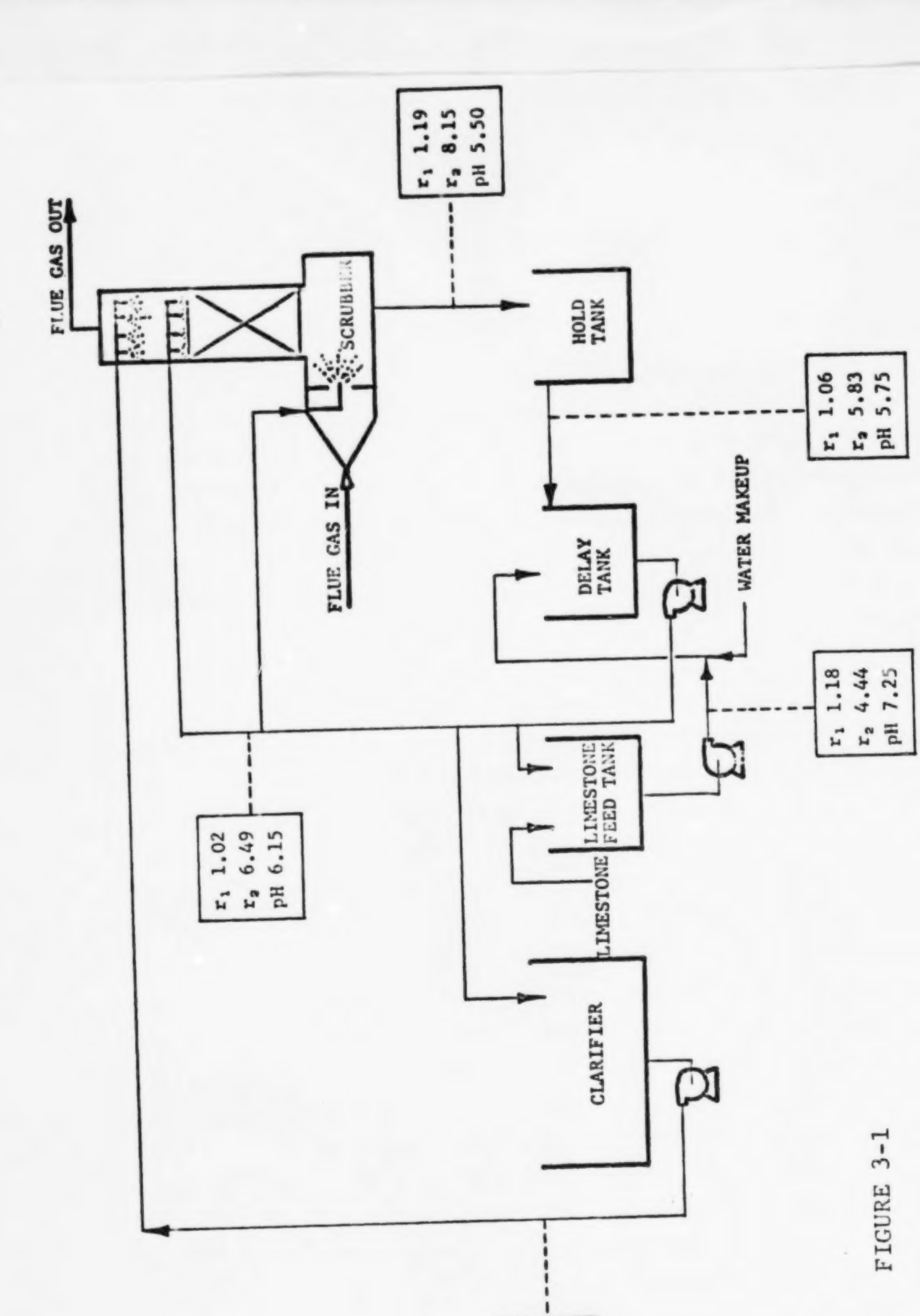
FLUE GAS OUT
SCRUBBER
FLUE GAS IN
HOLD TANK
r_1 1.19
r_2 8.15
pH 5.50
r_1 1.06
r_2 5.83
pH 5.75
DELAY TANK
WATER MAKEUP
r_1 1.18
r_2 4.44
pH 7.25
LIMESTONE FEED TANK
LIMESTONE
r_1 1.02
r_2 6.49
pH 6.15
CLARIFIER
r_1 1.35
r_2 1.68
pH 7.22

FIGURE 3-1

supersaturation with respect to calcium sulfate and r_2 be the relative supersaturation with respect to calcium sulfite, i.e.,

$$a_{Ca^{++}}a_{SO_4^=}/K_{sp_{CaSO_4}} \quad \text{and} \quad a_{Ca^{++}}a_{SO_3^=}/K_{sp_{CaSO_3}}$$

respectively. Using analytical chemistry methods described by K. Schwitzgebel (Paper No. 9a) the molalities at appropriate points in the system were measured. Using a programmed equilibrium model, activities of the ionic species were calculated and it was thus possible to describe r_1 and r_2 in any piece of equipment in the system. These values of r_1 and r_2 are given in Figure 3-1.

From the figure it can be seen that the slurry from the scrubber is caught in the hold tank. In the hold tank r_1 and r_2 decrease (de-supersaturation occurs). The hold tank overflows into the delay tank. Here further de-supersaturation occurs and r_1 becomes almost unity. The highest value for r_1 occurs in the clarifier where there is a relatively long hold time in contact with the air and the solids settle out. The reason for this appears to be that the clarifier is a poor liquid-solid mass transfer device. The total sulfur in the clarifier (sulfite plus sulfate) stayed essentially the same which indicates that little or no precipitation occurs. However, since the solution is in contact with a large air volume for a relatively long time period, oxidation from sulfite to sulfate occurs. Therefore, r_1 increases and r_2 decreases. The same events apparently take place in the limestone feed tank where the total sulfur remained essentially constant but r_1 increased and r_2 decreased.

From Figure 3-1 it can be seen that r_1 for calcium sulfate stays below the critical value of 1.3 to 1.4 in every part of the system. On the basis of these values of the relative supersaturation we would predict that calcium sulfate scale formation would not take place. A possible exception would be the clarifier outlet. The pilot plant observations are in agreement with our predictions in that no sulfate scale formation occurred.

Since the laboratory investigations for the calcium sulfite system have not yet been conducted there is no critical value of r_2 with which to compare the pilot plant values. The pilot plant data showed however that a value of r_2 up to at least 8 can be tolerated without the formation of calcium sulfite scale. In addition there is probably some value of r_2 above which sulfite blinding occurs in the system.

4.0 SUMMARY

Laboratory investigations and pilot plant observations indicated that sulfate scale-free operation will occur at values of relative supersaturation of less than 1.3. Pilot plant observations also indicated that sulfite scale-free and blinding-free operation occurs at values of relative supersaturation with respect to calcium sulfite less than 8.

These types of information are required for use in the design procedure. After heat and material balances have been made throughout a system, the scaling potential indicators can be used to predict operability with regard to scale formation.

ACKNOWLEDGEMENTS

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SAMPLING AND ANALYTICAL METHODS

J.A. Dorsey, Chairman

Participants:
Klaus Schwitzgebel
E.A. Burns and A. Grunt
Terry Smith and Ronald Draftz
Terry Smith and Hsing-Chi Chang
R.M. Statnick and J.A. Dorsey
Gene W. Smith

SUMMARY

SAMPLING AND ANALYTICAL METHODS

J.A. Dorsey, Chairman

The concluding session of the symposium dealt with the measurements programs developed primarily for the EPA prototype scrubber tests at the TVA Shawnee Steam Generating Station in Paducah, Kentucky. The methods are also applicable to other lime/limestone process development studies. The EPA program is designed to acquire extensive data on the composition of the process streams under varying operating conditions. The data will be utilized to perform a complete evaluation of the process chemistry, define operational problems, and model the process. This program results in a requirement for extensive sampling and analysis with a high degree of accuracy. While the basic chemistry of the process is rather straightforward, in actual operating practice the system presents a three-phase system that does not achieve equilibrium in the scrubber pass. This failure to achieve equilibrium (coupled with reactions producing undesirable soluble species, side reactions producing shifts in the sulfite-sulfate oxidation rates, and potential scale-producing species) presents significant sampling and analytical difficulties.

Sampling problems were discussed in the papers by K. Schwitzebel and by G. Burns as they relate to separation of the liquid and solid phases in the unstable slurry from the scrubber downcomer. Several techniques were devised, one based on centrifugal separation followed by filtration and one employing only filtration. Both of these techniques provide separations in less than 15 seconds. Sampling techniques for gaseous and particulate species in the gas phase were discussed in papers by R. Draftz and by R. Statnick.

Characterization of the slurry components requires analysis of nine ionic species in both the liquid and solid phases. This produces a laboratory load of over 450 analyses per day. K. Schwitzgebel discussed accurate referee methods and manual field methods for the required analysis. G. Burns presented evaluations of instrumental methods and development of on-line monitors for the slurry solids and liquor samples.

The gas-phase analysis of sulfur and nitrogen oxides was discussed by R. Statnick. An evaluation of instruments suitable for continuous monitoring was presented. The development of a manual-size selective particulate sampling system for suspended particulate in the gas phase was described by R. Draftz.

Finally, a discussion of the proposed EPA methods for new source performance standards was presented by G. Smith. These methods or an equivalent will be required to define compliance with emission standards. Hence, anyone developing control systems should incorporate similar tests into his program,in addition to the tests being used for engineering analysis. A copy of the December 23, 1971, Federal Register, containing the final version of the methods, is included with the symposium papers.

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DEVELOPMENT AND FIELD VERIFICATION OF SAMPLING AND ANALYTICAL METHODS FOR SHAWNEE

By:
Klaus Schwitzgebel

Presented at:

SECOND INTERNATIONAL LIME/LIMESTONE
WET SCRUBBING SYMPOSIUM
8-12 November 1971
Sheraton-Charles Hotel
New Orleans, Louisiana

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Division of Control Systems

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1.0 INTRODUCTION

The work presented here describes the analytical and sampling techniques for the forthcoming test facility at Shawnee. One of the main objectives is the collection of engineering design information for lime/limestone based SO_2 removal processes. Therefore, the demand for accuracy of the analytical chemistry methods is more stringent than the demand for accuracy in control processes.

The problem areas in analyzing unstable slurry streams are sampling, sample handling and analysis. Two kinds of analytical methods were selected, referee methods (used also as back-up) and rapid field methods.

The ultimate use of the analytical results is for chemical engineering purposes. The chemical engineer uses the data to describe:

- vapor-liquid mass transfer characteristics in the scrubber
- solid-liquid mass transfer rates throughout the system
- scaling potential

A mathematical description of the reaction kinetics of the mass transfer steps as a function of the liquor composition is a prerequisite for the process engineering of limestone based sulfur dioxide removal processes. The driving force term in these rate equations is a function of the difference between actual and equilibrium conditions. The driving force term for liquid-solid mass transfer is a function of the difference between actual and equilibrium activities. The driving force term for gas-liquid mass transfer is a function of the difference between actual and equilibrium vapor pressures.

The solutions are non-ideal. Concentrations are not suitable quantities for describing the driving forces. Thermodynamic concentration, or activity, must be used. Only the total amount of a species in solution is measured by chemical analysis. The activities of the species of interest differ markedly from chemical analysis values due to complexation and the deviation of the solution from ideality. An example is given showing how the activities of the important species can be extracted from the results of the chemical analyses.

2.0 PROBLEM DEFINITION

The basic equipment arrangement for limestone injection wet scrubbing (LIWS) processes is shown in Figure 1. The three streams entering the system are flue gas, particulates and make-up water. Three streams leaving the unit are cleaned stack gas, solid waste products, and scrubbing liquor. The composition of the incoming streams provides a means of predicting the liquor composition on a qualitative basis. The important species in the LIWS process are:

Group I
calcium
sulfite
sulfate

Group II
sodium
potassium
magnesium
chloride
nitrate
nitrite
carbonate

Group III
trace elements
iron
cobalt
nickel
copper
manganese

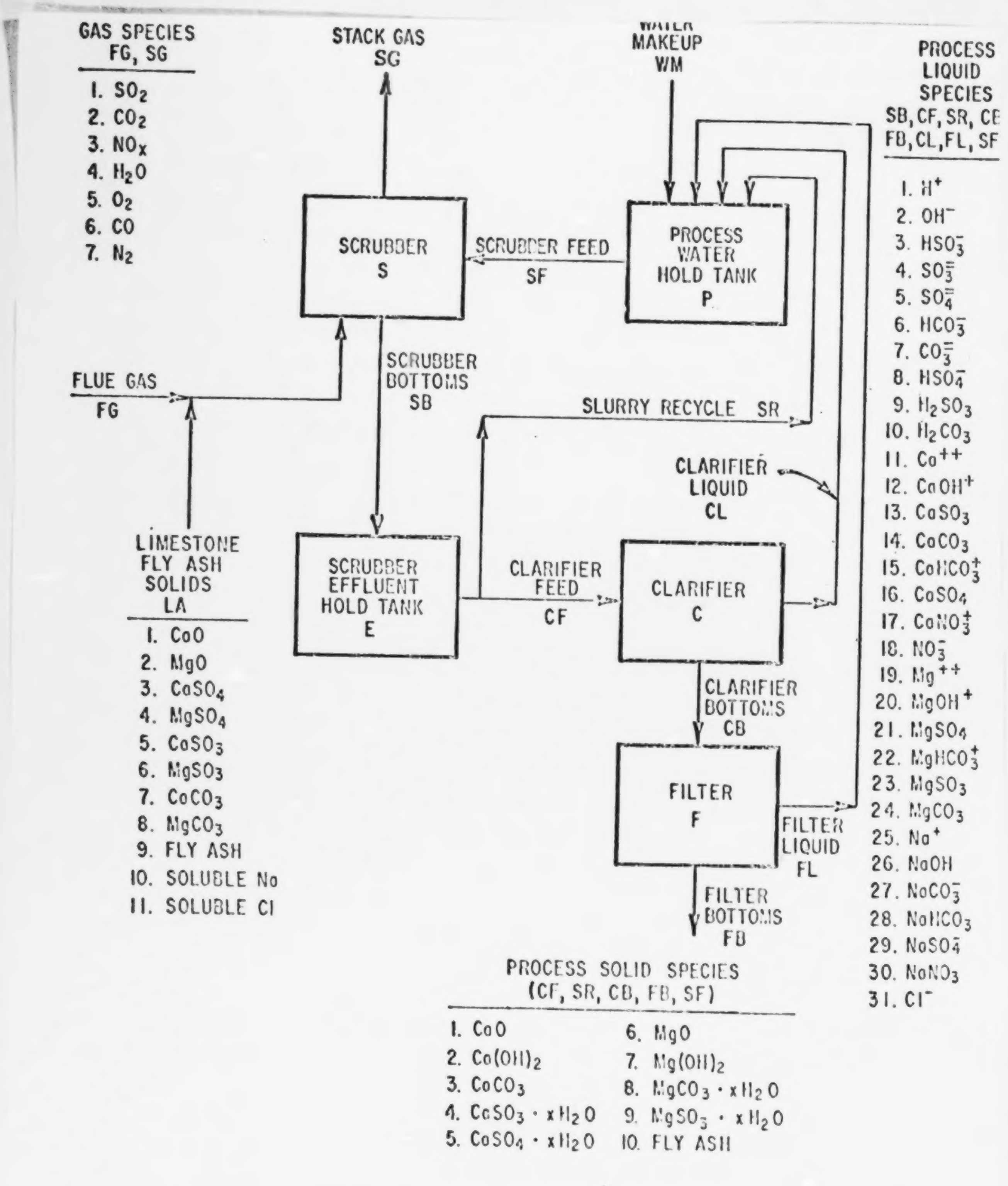


FIGURE 1 WET SCRUBBING SCHEME

The components listed in Group I are the most important. They dominate the process by participating in the gas-liquid and liquid-solid mass transfer steps. The species listed under Group II contribute to the process performance in three ways. First, they influence solubilities which are dependent on the ionic strength of the solution. Second, they form ion pairs with Group I compounds. Finally, they influence the driving force for the mass transfer rates. The components in this group form very soluble compounds with the exception of magnesium hydroxide and calcium carbonate. In a closed loop operation there is a buildup of the soluble compounds, since the only stream in which they can leave the scrubbing unit is the liquor adherent to the solids. This fact must be kept in mind when selecting analytical methods. The procedures must give accurate results in those cases where the soluble species build up to a high level. The implications for the selection of methods for sulfate and sulfite will be discussed later.

The third group is comprised of species leached from the fly ash and impurities in the limestone. The concentration of these elements is never very high, since it is limited by the solubility of the hydroxides in the alkaline parts of the scrubbing unit. Their importance is based on the fact that they are excellent catalysts for sulfite oxidation, even if present in the parts per billion range.

The process simulations, discussed earlier by D. M. Ottmers, Paper #1c, gave a valuable basis for estimating anticipated concentration ranges. Estimation was necessary since no data on a closed loop system operated over an extended period of time were available at the time of analytical method development.

As a general rule, the higher the accuracy demand of an analysis, the higher are its costs. This fact raises the question as to the ultimate use of the analytical results. The accuracy requirements for routine, day-to-day operation are less stringent than the requirements for process analysis. One key objective of the forthcoming tests at Shawnee is the collection of engineering design information. From an engineering point of view the following areas are of ultimate interest:

- gas-liquid mass transfer rates in the scrubber
- dissolution and precipitation rates as function of liquor composition
- scaling potential.

The driving force term in the mass transfer equations describing these rates is a function of the difference of the actual process condition and the equilibrium condition of the system. In other words, the rates are a function of the difference of two activity expressions. The closer the system operates to equilibrium the more severely analytical errors will influence extracted rate correlations. For LIWS processes the analyses of the species listed in Group I are therefore the most important. Error propagation calculations showed that the error in these analyses should not be greater than about 2%. The concentration of the species influencing the ionic strength (Group II) must be known within about 4%. The accuracy requirements for the trace elements effective as catalysts are still less stringent. Twenty to fifty percent is considered to be sufficient.

The analytical results are influenced by three steps:

- solid-liquid separation
- sample handling
- actual analysis

These problem areas will be discussed next.

3.0 SAMPLING

The scrubbing system can be divided into an acidic and a basic part. The environment is acidic in the scrubber itself and in the pipe between the scrubber and the effluent hold tank. The solutions circulated in the rest of the system are alkaline. For sampling purposes it should be noted that the scrubbing slurry, especially in the acidic part of the system, is not in thermodynamic equilibrium. The sorbent tends to dissolve and sulfite and sulfate tend to precipitate. The technique often used to sample this stream is collection of a slurry sample in a beaker and filtration through a Buchner funnel. This technique results in only semi-quantitative results for the follow-on chemical analysis for three reasons:

- loss of acidic gases (SO_2, CO_2) especially if a vacuum is used

- solid-liquid mass transfer during the sampling procedure

- sulfite oxidation by air oxygen.

Because of these sources of error most of the pilot plant data presently available must be considered to be qualitative in nature and not suitable for the extraction of engineering design information. In-line, positive pressure filtration was the sampling method selected after field tests at several pilot units (see Figure 2). The sampling apparatus consists of a positive pressure pump, a membrane filter holder and lines and valves to control sampling and purge rates. Flow rates used in the tests were about 1300 ml/min. The residence time of the slurry is about 2.3 seconds in the filter and approximately seven seconds in the entire sampling equipment.

The degree of mass transfer in the filter cake, which is by nature a good contacting device, was checked by taking consecutive samples and plotting the chemical analysis results as a function of the filtered volume. Extrapolation to zero volume of filtrate represents the true aqueous phase composition. With the exception of carbonate, the amount of solids dissolved or precipitated in the filter cake was within the experimental error of the chemical analyses.

Loss of acidic gases is avoided by the positive pressure filtration, and air oxidation of sulfite is prevented by fixing the sample immediately.

4.0 FIXING OF THE FILTERED LIQUID

After filtration care must be taken that the liquid samples do not undergo further change. This is especially true for the sulfite analysis. Sulfite losses can occur by :

- evaporation from acidic samples
- oxidation by air oxygen
- interaction with nitrites

Nitrites can be formed by absorption of NO and NO_2 from the flue gas. All three sulfite losses can be avoided by quenching the sample in a solution of pH = 6 with known iodine content.

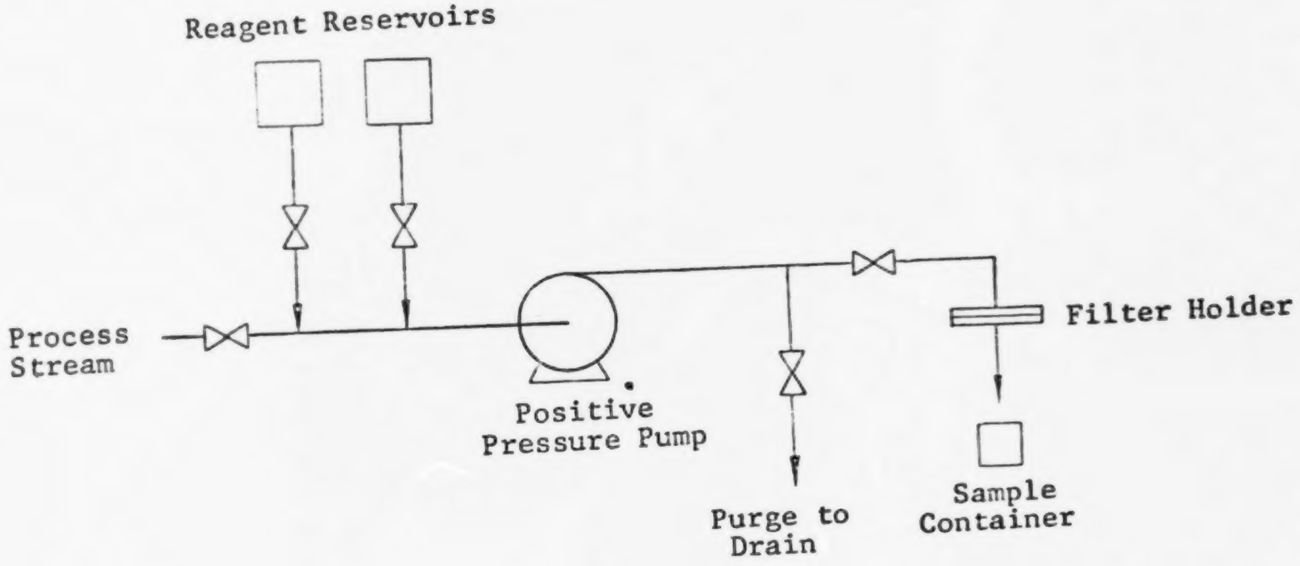


FIGURE 2

Typical Slurry Sampling Train

Carbonate losses from acidic liquid can be avoided by quenching the sample in a solution of pH = 10. EDTA must be added to the buffer in order to avoid calcium carbonate precipitation at this pH.

Sulfate in the presence of sulfite is determined as the difference between the total sulfur and the sulfite sulfur. In order to avoid sulfite losses and sulfate precipitation the sample for total sulfur analysis is quenched in a H_2O_2-water solution. Hydrogen peroxide oxidizes the sulfite. Dilution with distilled water prevents sulfate precipitation in the sample bottle.

5.0 LIQUID PHASE ANALYSIS METHODS

The literature was surveyed through 1970 for analytical methods which might be applicable to solutions of interest. The sources consulted were:

- Kolthoff and Elving, "Treatise on Analytical Chemistry"
- Biannual Reviews on Analytical Chemistry
- 1969 Book of ASTM Standards
- FWPCA Methods for Chemical Analysis of Water and Wastes
- Chemical Abstracts
- Pertinent Original Articles

Promising methods for application to the analysis of wet scrubbing liquors were checked in the laboratory and through visits to manufacturers. Two types of analysis methods were sought: referee (and back-up) methods and rapid routine procedures.

5.1 Back-Up Methods

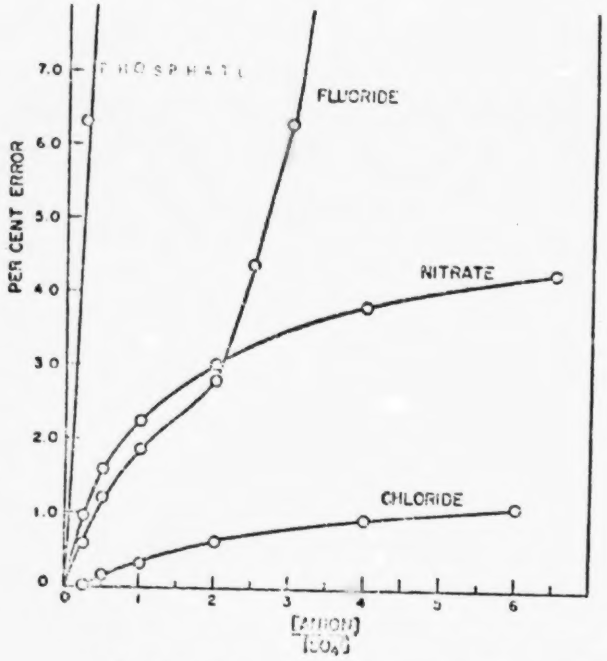
The literature review revealed that the choice of method for sulfate, calcium and sulfite in the key or Group I species is rather limited. The methods published for sulfate analysis can be divided into five groups.

1. Gravimetric Procedure
2. Direct Titrimetric Procedures
3. Indirect Titrimetric Methods
4. Colorimetric Techniques
5. Turbidimetric Procedures

All these methods, with few exceptions, are based on the formation of insoluble barium or lead sulfate. They all, therefore, show the same potential interferences, namely, coprecipitation errors, occlusion of foreign salts, and errors due to supersaturation The techniques most widely used are the gravimetric method (ASTM referee method), direct titration in a water ethanol mixture using $Ba(ClO_4)_2$ or $BaCl_2$ as titrant and thorin as end point indicator, the barium chloranilate method (FWPCA method), and the turbidimetric technique.

The gravimetric procedure was rejected for two reasons. First, it is extremely time consuming, and second, there are interferences expected in scrubbing solutions with high salt background. Alkali metals cause errors due to occlusion. Calcium causes serious errors due to coprecipitation. Nitrate is reported to cause errors by occlusion. The occlusion and coprecipitation problems due to cations can be avoided by use of ion exchange resins.

The direct titration using thorin as end point detector was rejected due to severe anion interferences. Figure 3 shows the errors caused by several common anions.



Results of titration of sulfate in presence of different concentrations of common anions

FIGURE 3

Reference: Fritz, J. S., and S. S. Yamamura, Anal. Chem., 27, 1461-1464 (1955).

Compensation for these anion interferences can be made by standardizing the titrant solution with a H_2SO_4 standard containing the foreign ions at a concentration corresponding to that of the unknown solution. This technique may be useful in routine analytical work, but is not acceptable for sulfate determination in varying environments.

The turbidimetric sulfate determination is recommended by ASTM mainly as a control procedure where concentration and type of impurities present in the water are relatively constant. Kelly and Baldwin [Chem. & Ind., 1283-1285 (1969)] automated this technique using an autoanalyzer. They report results more consistent than with manual operation. Compared with gravimetric techniques, however, they found deviations of ± 10%, which is unacceptable.

Extensive laboratory effort was devoted to the barium chloranilate method recommended by FWPCA. The laboratory results revealed nitrate and chloride interference if these anions are present at higher concentrations as well as a critical dependence on pH. In addition, inconsistencies were found if different batches of reagents were used. The time required for complete reaction and precipitation to take place as well as the time required to separate the very fine barium sulfate precipitate from the acid chloranilate solution gave very little hope for complete, fast automation of the method for very accurate determinations. These precipitation difficulties were one of the main reasons that the barium chloranilate method was also abandoned by Technicon.

The method ultimately adopted is an ion exchange alkalimetric procedure. Sulfate in aqueous solutions is determined as sulfuric acid after passage of the sample through a hydrogen form cation exchange resin. The aqueous acid mixture obtained after the cation exchange is evaporated to a few milliliters on a steam bath or a hot plate. After this step all the acids and the water are driven off by evaporation at 75°C. Only H_2SO_4 and other nonvolatile acids such as H_3PO_4 remain. If H_3PO_4 is absent, the sulfuric acid can be titrated directly. If H_3PO_4 is present, H_2SO_4 is driven off at 275°C and the H_3PO_4 is determined by alkalimetric titration. The method is free from cation interference.

Phosphoric acid presents the most severe anion interference. This acid must be determined separately if it is present in large amounts. Table 1 compares the results obtained with the volumetric method to the results obtained with the gravimetric procedure. The method was checked in Radian's laboratory using high salt backgrounds. Laboratory results are presented in Table 2. Results in analyzing field samples agreed within 2% with the X-ray fluorescence technique discussed later.

The methods for sulfite determination in the presence of nitrite are also rather limited. The normal iodine thiosulfate procedure gives erroneous results due to nitrite-sulfite interaction at the low pH values used in the procedure. The best method found was to quench the filtered liquid in a buffer of pH = 6 containing a known amount of iodine. The back titration must be done at this pH value with arsenite instead of thiosulfate, since thiosulfate is partly oxidized to sulfate in the presence of nitrite at pH = 6. A dead-stop technique for the end point detection was chosen. At low sulfite concentrations this leads to better results than the starch indicator normally used.

The most convenient method for the determination of the third species in Group I, calcium, was found to be atomic absorption. A 5% HCl, 1% $LaCl_3$ solution used to dilute the samples into the optimum range for A.A. measurement was found to suppress all the interferences.

Table 3 summarizes the referee methods found to be most suitable for scrubbing liquor anlaysis.

TABLE 1
GRAVIMETRIC AND VOLUMETRIC DETERMINATIONS OF SULFATE IN VARIOUS SAMPLES

	Sulfate Found, mg/ℓ	
Sample[a]	Gravimetric	Volumetric
1	427	426
2	421	419
3	391	390
4	188	188
5	167	165
6	161	162
7	104	101
8	96.5	95.7
9	87.5	87.0
10	60.2	59.7
11	39.4	40.1
12	27.0	26.4
Sea Water[b]		
(one sample)	2,650	2,630
	2,640	2,630
	2,640	2,630
Sewage[c]		
(one sample)	125	124
	124+	124
	124	124

---

a. Natural waters (surface streams, wells, reservoirs, etc.)

b. Diluted 1 to 50 prior to ion exchange.

c. Filtered and brominated prior to ion exchange.

TABLE 2

DETERMINATION OF SULFATE IN LIMESTONE INJECTION SIMULATION SOLUTIONS USING DIFFERENT RESINS

Exper. #		SAMPLE	ml 0.0502N NaOH used	m mole $SO_4^=$ Theory	Exper.	Percent Error
1	Amberlite	10 ml Simulation Soln.*	3.92	0.0990	0.0984	-0.7
2		" "	3.94	"	0.0989	-0.1
3		" plus H_2O_2	3.96	"	0.0994	+0.4
4		" plus Na_2SiO_3	3.95	"	0.0991	+0.1
5	Dowex	10 ml Simulation Soln.*	3.95	"	0.0991	+0.1
6		" "	3.95	"	0.0991	+0.1
7		" plus H_2O_2	3.96	"	0.0994	+0.4
8		" plus Na_2SiO_3	3.96	"	0.0994	+0.4
9	Rexyn	10 ml Simulation Soln.*	3.95	"	0.0991	+0.1
10		" "	3.96	"	0.0994	+0.4
11		" plus H_2O_2	4.04	"	0.1014	+2.3
12		" plus Na_2SiO_3	3.96	"	0.0994	+0.4
13		10 ml Pure K_2SO_4 Soln.	3.97	"	0.0996	+0.6

Resin column dimensions: 1.2 cm I.D. x 18 cm high.
Resins used: Amberlite CG-120, Dowex 50W, and Rexyn 101.
All were 100-200 mesh size.

* Simulation solution contained:
0.009904 M K_2SO_4
0.150 M $Ca(NO_3)_2$
0.100 M NaCl
0.05 M HCl

Samples 3, 7, and 11 contained 2.2 m moles H_2O_2 which was added as 5 drops of 30% solution.
Samples 4, 8, and 12 contained 0.1 m mole Na_2SiO_3 which was added as 1 ml of 1 M solution.

TABLE 5

REFEREE METHODS AND NECESSARY EQUIPMENT

Species Sought	Referee Method	Instrumentation	Optimum Concentration range ppm	Accuracy
Na^+	Atomic Absorption	A.A. Spectrophotometer, Lamps, Atomatic Diluters	≤1.5	3%
K^+	Atomic Absorption		≤6	5%
Ca^{++}	Atomic Absorption		≤7	2%
Mg^{++}	Atomic Absorption		≤0.7	2%
SO_2	Iodometric Dead Stop Titration	u amp Meter, Electrodes, 25 ml Buret	3-30 (mg in sample)	1-2% (depending on nitrite conc.)
SO_3	Ion Exchange, Alkalimetric	Drying Oven, Precision Buret, 10 Ion Exchange Columns (automatic titrator)	1000-2000	1%
CO_2	Evolution Method	Oceanographic International Instrument	100	2%
Cl^-	Mercurimetric Titration (potentiometric)	Precision Buret (automatic titrator)	300-700	<2%
Total N	Reduction to NH_3 and Distillation	Glass Apparatus	15-25 (mg in sample)	1%
NO_3^-	U.V. or Colorimetric with Chromotropic Acid	Spectrophotometer	100-5000	3%
NO_2^-	U.V.	Spectrophotometer	100-1000	3%
Trace Metals: Cu, Fe, Mn, Co	Atomic Absorption	Lamps	15-20 ppb	20%
Ni	Atomic Absorption	Lamp	50-200 ppb	10%

5.2 Routine Field Methods

The selection of routine field methods was based on the type and number of analyses per day required at peak load operation. This breakdown is shown in Table 4. Table 5 gives the time requirements per day in the event that the back-up methods are used. Duplicate analyses were assumed if not indicated otherwise. The last column in Table 5 shows the total man-minute/day necessary for each type of analysis. The costs show the following pattern: Total S > Ca > Mg > SO_2 > CO_2 > Cl = K, with total sulfur being the most expensive determination.

X-ray fluorescence appeared to be a technique which cut the expenses drastically. However, no data were found in the literature describing the use of this technique in analyzing liquors of the composition encountered in lime/limestone based scrubbing processes. Figure 4 shows the principle of this technique. The specimen is radiated by a primary X-ray source. The elements present in the sample emit characteristic secondary emission lines whose wavelengths and intensities are measured using an analyzer crystal and a counter.

Quantitative X-ray fluorescence analysis is subject to interferences as are most of the other analytical procedures. The intensity of the emission line of an element can be reduced or increased by the other elements present in the sample. An increase is observed if secondary excitation occurs. A reduction of intensity is caused by absorption effects. Correction factors must therefore be determined and the measured intensities corrected.

Tables 6 and 7 present preliminary results in analyzing simulated scrubber solutions for sulfur and calcium. The RMS errors for the two most important key species are quite acceptable. Preliminary results indicate that chlorine, potassium , and magnesium also can be determined by this technique.

TABLE 4

NUMBER OF ANALYSES PER DAY AT PEAK LOAD OPERATION

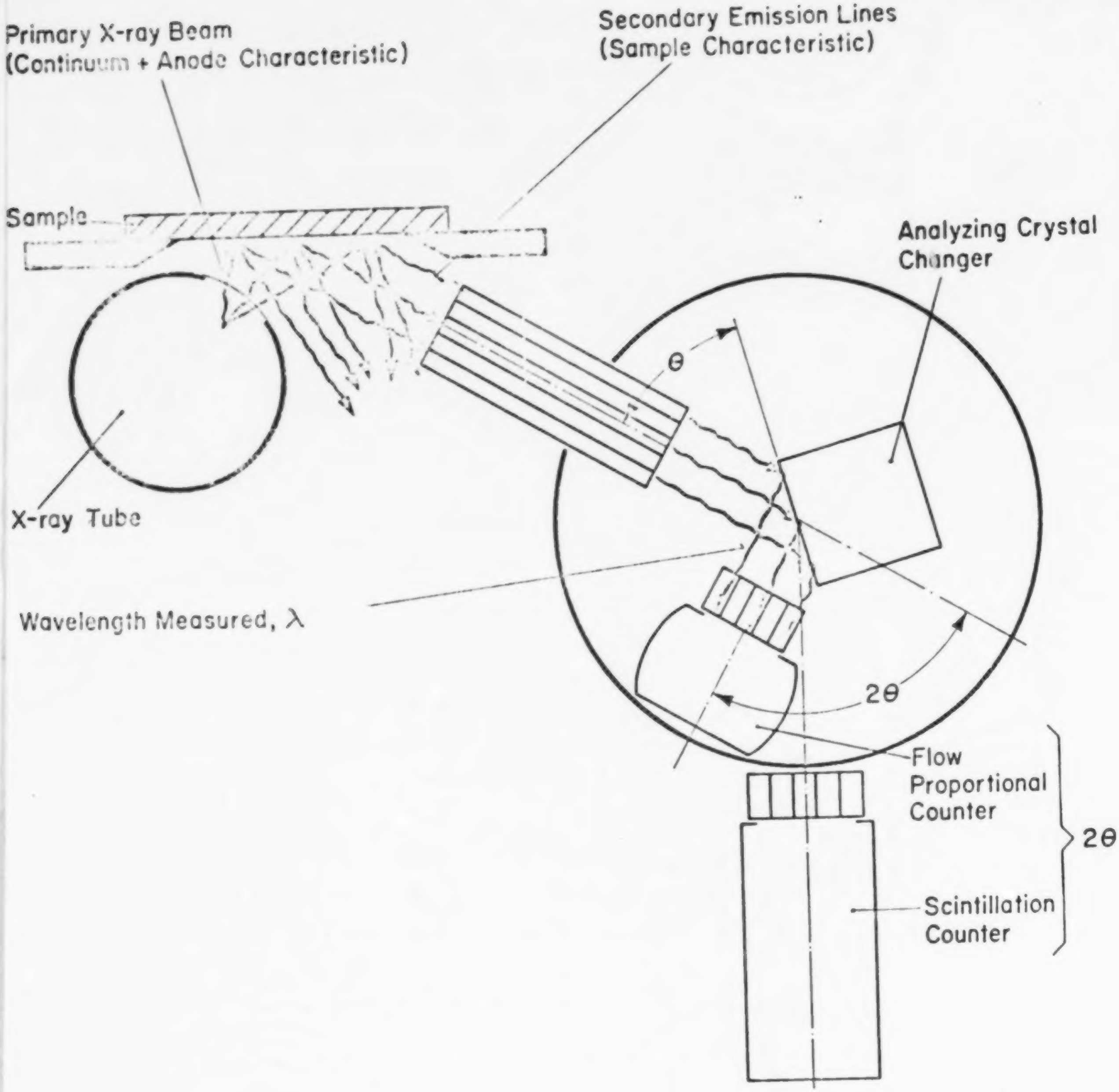
Species Sought	Number of Analyses at Steady State	Analyses During Line Out	Total
Ca^{++}	53	27	80
Mg^{++}	48	27	75
K^{+}	9	27	36
Na^{+}	9		9
Total S	53	27	80
SO_2	36	27	63
Cl^{-}	9	27	36
CO_2	53		53
Total N	9		9
NO_2^-	9		9
NO_3^-	9		9
			459

TABLE 5

ESTIMATED TIME REQUIREMENTS USING REFEREE METHODS

Species Sought	Method	Time/Analysis (min)	Analyses/Day	Total Man-Min./Day
Na^+	A.A.	15	18	270
K^+	A.A.	15	72	1,080
Ca^{++}	A.A.	15	160	2,400
Mg^{++}	A.A.	15	150	2,250
SO_2	Dead Stop, Iodometric	15	126	1,890
Total S	Ion Exchange, Alkalimetric	30	160	4,800
CO_2	Evolution Method	15	106	1,590
Cl^-	Mercurimetric (potentiometric)	15	72	1,080
Total N	Reduction to N + Distillation	30	9(single determin.)	270
NO_2, NO_3	U.V. Technique	20	9(single determin.)	180
				15,810 Min./Day

or 263.5 Man-Hours/Day



$$\boxed{n \cdot \lambda = 2d \cdot \sin\theta}$$

FIGURE 4

TABLE 6

Results of Sulfur Analyses Corrected for Nitrogen and Magnesium Interference Only

Sample Number	Sulfur Content (mmoles/ℓ)	Corrected Values Instrument I	% Error	Instrument II	% Error
14	25	25.3	1.2	25.5	2.0
15	25	25.2	0.8	25.1	0.4
13A	25	24.7	-1.2	----	----
16	25	24.6	-1.6	24.8	-0.8
17	25	24.9	-0.4	25.6	2.4
18	25	25.2	0.8	25.5	2.0
19A	50	48.9	-2.2	----	----
20	50	49.2	-1.6	52.2	4.4
21	50	49.0	-2.0	50.6	1.2
22	50	49.2	-1.6	50.0	0.0
23	50	49.7	-0.6	51.8	3.6
24	50	50.2	0.4	49.9	-0.2
25	50	49.6	-0.8	49.4	-1.2
26	50	49.9	-0.2	50.8	1.6
27	50	49.7	-0.6	50.0	0.0
28	50	50.3	0.6	50.9	1.8
29	50	50.4	0.8	49.9	-0.2
30	50	51.4	2.8	53.0	6.0
		RMS =	1.8	RMS =	2.4

TABLE 7

Results of Calcium Analyses Corrected for Nitrogen, Magnesium, Potassium, Chlorine, and Sulfur Interferences

		Corrected Values			
Sample Number	Calcium Content (mmoles/ℓ)	Instrument I	% Error	Instrument II	% Error
86	10	10.0	0.0	9.7	3.0
77	25	25.0	0.0	25.0	0.0
78	25	25.0	0.0	25.0	0.0
79	25	25.0	0.0	24.9	-0.4
80	25	25.0	0.0	25.0	0.0
81	25	25.0	0.0	24.8	-0.8
82	25	25.0	0.0	24.6	-1.6
90	50	50.3*	0.6	50.2	0.4
91	50	50.2*	0.4	49.8	-0.4
92	50	50.0*	0.0	49.2	-1.6
		RMS =	0.2	RMS =	1.3

*50 mmoles/ℓ Calcium values exceed linear range

Table 8 compares the results of the proposed referee method and of X-ray fluorescence in analyzing total sulfur in samples taken from different streams at TVA's Colbert Station pilot plant. The agreement can be judged as being good.

A big advantage of X-ray fluorescence not yet mentioned is the speed of analysis, especially if a minicomputer is used to perform the matrix interference corrections. The estimated savings in time for the Shawnee tests are reflected in Table 9. The man-minutes/day are cut by a factor of four as compared to the referee methods.

6.0 SOLID ANALYSIS

The solid analysis comprises three steps:

- phase identification
- solids dissolution
- analysis of the liquid phase.

The phase identification of crystalline compounds collected on the filter previously described is most conveniently done using X-ray diffraction. Important solid species (other than fly ash) potentially present are:

Calcium Compounds

1. CaO
2. $Ca(OH)_2$
3. $CaCO_3$ (aragonite)
4. $CaCO_3$ (calcite)
5. $CaSO_3 \cdot \frac{1}{2}H_2O$
6. $CaSO_4 \cdot 2H_2O$
7. $CaSO_4 \cdot \frac{1}{2}H_2O$
8. β-$CaSO_4$
9. γ-$CaSO_4$

Magnesium Compounds

1. MgO
2. $Mg(OH)_2$
3. $MgCO_3 \cdot 3H_2O$
4. $MgSO_3 \cdot 3H_2O$
5. $MgSO_3 \cdot 6H_2O$

TABLE 8

CHEMICAL AND X-RAY ANALYSIS OF FIELD SAMPLES TAKEN AT COLBERT STATION

Sample Designation	S(mmoles/ℓ) (Chemical Analysis)	X-Ray Fluorescence mmoles/ℓ	% Difference
(1) VR Outlet (inhibited) 4/6/71	27.5	26.9	-2.2
(2) To CF Scrubber 4/6/71	33.0	33.6	+1.8
(3) To VR Scrubber 4/6/71	24.6	24.8	+0.8
(4) CF Inlet Liquid 4/7/71	20.2	19.8	-2.0
(5) Tank F16 Liquid 4/7/71	20.5	20.9	+2.0
(6) CR Scrubber Outlet 4/6/71	37.2	38.2	+2.8

TABLE 9

INSTRUMENTATION AND MANPOWER LOAD USING X-RAY FLUORESCENCE

(Basis: Table 3, however duplicate analyses)

Species Sought	Field Method	Min./Analysis	Analyses/Day	Total Man-Min./Day
Na^+	Atomic Absorption	10	18	180
K^+ Ca^{++} Mg^{++} Total S Chloride	X-Ray Fluorescence	120 sec. He Flush 40 sec. Ca 40 sec. K 40 sec. Cl 80 sec. S 160 sec. Mg 480 sec. = 8 min.	160 Based on Maximum Number of Analyses Necessary for Ca and S	1,280
SO_2	Dead Stop Iodometric	10	126	1,260
CO_2	Evolution Method	10	106	1,060
Total N	Reduction and Distillation	30	9 (single determin.)	270
NO_2^- NO_3^-	U.V. Technique U.V. Technique	20	9 (single 9 determin.)	180
				4,230 Min./Day
				or 70.5 Man-Hours/Day

The characteristic diffraction patterns for these compounds are listed in the "Inorganic Index to the Powder Diffraction File".

The diffraction patterns of the collected solids can be obtained using a film or a goniometer technique. The principle of these methods is outlined in Figures 5 and 6.

The next step in solids analysis is the chemical analysis of the individual compounds. Carbonate is determined on a weighed sample by the evolution technique. Sulfite is determined by dissolving a weighed sample in an iodine solution of known iodine content. Calcium, magnesium and total sulfur are determined in a sample dissolved in a weak mineral acid containing H_2O_2 for the oxidation of sulfite. The total calcium, magnesium, and sulfate in solution can then be determined by X-ray fluorescence or the referee methods described earlier. Typical analysis results are presented in Section 7.

7.0 FINDINGS ON PILOT PLANT STUDIES

The sampling, sample handling and referee methods were developed and tested by analyzing data from several pilot units. Samples were collected during

- OAP in-house studies
- pilot plant runs at the Tidd Plant in Brilliant, Ohio
- pilot plant runs at Key West
- pilot plant studies at TVA's Colbert Steam Plant
- pilot plant studies at Shawnee

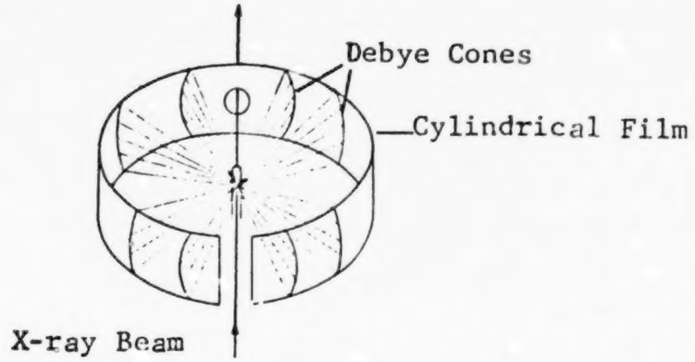


FIGURE 5 - Principle of the Debye-Scherrer Method Using a Cylindrical Camera

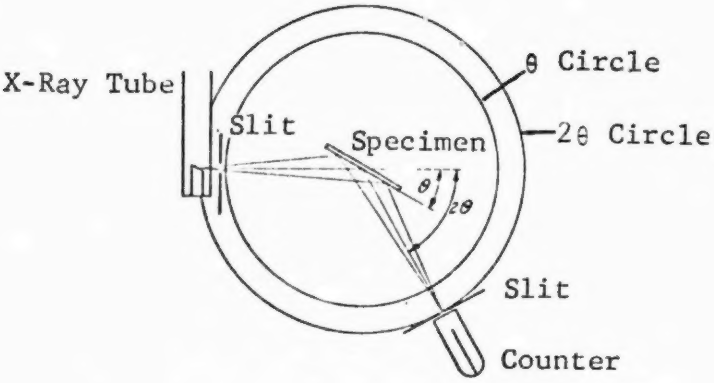


FIGURE 6 - Use of the Goniometer Technique to Obtain X-Ray Spectra from Powders. The intensity of the reflected radiation is monitored by a counter and plotted with a strip chart recorder as function of the angle 2θ. The specimen is rotated with half the speed of the counter.

Results will be presented for the pilot studies at TVA's Colbert steam plant. The system arrangement at Colbert is shown in Figure 7. Samples were taken and analyzed at the scrubber effluent (sample point 2), scrubber spray (sample point 1), effluent hold tank F-12 overflow (sample point 3), and the process liquor tank F-13 (sample point 4). The results of the liquid and solid phase analyses are shown in Tables 10 and 11. The buildup of inerts is very small in this arrangement since most of the fly ash was removed by the raw water spray.

The accuracy of the methods is reflected in the imbalance.

$$\sum\left(m_i \cdot z_i\right)_{pos} - \sum\left(m_i \cdot z_i\right)_{neg}$$

The pH measurements and analytical results shown in Table 10 were used to calculate this imbalance. The imbalance should ideally be zero for zero errors in the analytical determinations. Another source of ionic imbalance is the presence of species for which no analysis was made.

The results of the solid phase analyses are presented in Table 11. The concentrations of the solid species add up to nearly 100% with exception of the solids of the scrubber spray which contains most of the fly ash. Compounds leached from the fly ash for which no analysis was made may be responsible for the low values found.

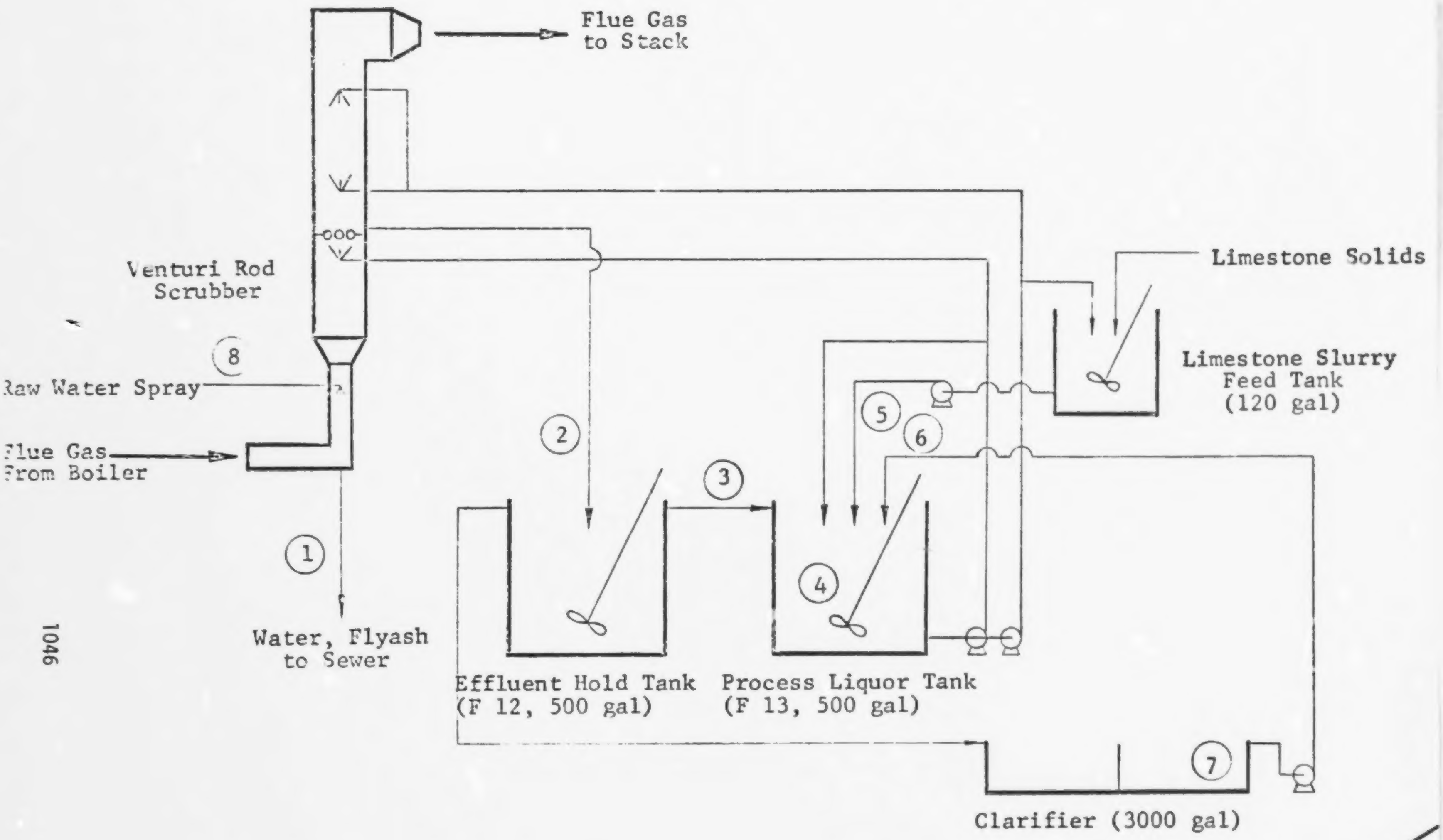


FIGURE 7 - TVA Limestone Wet Scrubber Pilot Unit

TABLE 10

RESULTS OF LIQUID SAMPLE ANALYSIS

Colbert Plant, Run 3 5/28/71

Sample Designation	Sample Point (See Fig. 7)	K	Na	Ca	Mg	Sulfite + Sulfate	Sulfite	Sulfate	CO_2	Cl	Total N	NO_3	Imbalance $\Sigma(m_i z_i)_{pos} - \Sigma(m_i z_i)_{neg}$ (mmoles)	pH	Temperature (°F)
Scrubber Effluent	2	0.28	0.49	32.7	12.4	43.4	10.0	33.4	3.07	9.3	3.50	.662	-2.69	5.67	101
Scrubber Spray	1	0.12	0.25	6.9	0.27	9.23	6.5	2.73	1.45	2.0	0.17		+1.78	3.19	102
F-12 Overflow	3	0.30	0.49	30.3	12.6	41.4	9.0	32.4	4.95	9.8	1.27	.723	-1.87	5.77	101
F-13 Recycle	4	0.29	0.48	29.9	12.7	39.0	5.6	33.4	3.93	9.2	1.23	.649	-1.12	5.96	101
Clarifier Overflow	6										0.94	.588			

NOTE: Concentrations are given in mmoles per liter.

TABLE 11

RESULTS OF SOLID SAMPLE ANALYSIS

Colbert Plant, Run 3, 5/28/71

Sample Designation	Sample Point (see Fig. 2.1)	Results of X-Ray Analysis	Weight of Analyzed Sample (mg)	Weight of Undissolved Solids	Slurry Concentration (g/l)	Analyses of Acid Soluble Material Concentration in m moles Per Gram of Solid								Solids Composition	
						Ca	Mg	Sulfite and Sulfate	Sulfate	Sulfite	Carbonate	Ca + Mg	Sulfate + Sulfite + Carbonate		
Scrubber Effluent	2	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ (Gypsum) 4. $CaSO_3 \cdot \frac{1}{2}H_2O$	1003	35	85.2	7.98	0.53	3.11	1.16	1.95	5.41	8.51	8.52	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	25.2% 20.0% 4.5% 48.7% 3.5% 101.9%
Scrubber Spray	1	1. $CaCO_3$ (Calcite) 5. $Ca(Al_2Si_2O_8) \cdot 4H_2O$ (possible) 6. SiO_2 (possible)	996	784	17.2	1.52	0.09	.076	.006	0.07	1.57	1.61	1.63	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	1.0% 0.1% 0.9% [illegible] [illegible] [illegible]
F-12 Overflow	3	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ 4. $CaSO_3 \cdot \frac{1}{2}H_2O$	1006	42	100	8.10	0.59	2.78	1.05	1.73	5.38	8.69	8.16	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	22.3% 18.1% 5.0% 53.2% 4.2% 102.8%
F-13 Recycle	4	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ $CaSO_3 \cdot \frac{1}{2}H_2O$ Unidentified Component Present in Significant Amounts	1014	44	87.9	7.85	0.51	3.44	1.40	2.04	5.00	8.36	8.44	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	26.3% 24.1% 4.3% 44.1% 4.3% 103.1%

8.0 USE OF THE RAW DATA

It was mentioned earlier that the results of the chemical analyses have no value per se. They gain their value in the chemical engineering framework within which they are used. Dominant points of interest are:

- mass transfer characteristics in the scrubber
- solid-liquid mass transfer rates
- scaling potential

Therefore, the data presented in Tables 10 and 11 must be processed further. As an example, suppose one wishes to predict the scaling tendency of the scrubber effluent given in Table 10. This task is solved by considering the ionic equilibria in the aqueous phase. The results of the chemical analysis listed in Table 10, the pH value and the temperature were used as inputs for computer calculations. The resulting activities of the individual ionic species for the scrubber effluent are listed in Table 12.

The activities of Ca^{++}, $SO_3^{=}$, and $SO_4^{=}$ are given as 7.25×10^{-3}, 1.22×10^{-4}, and 5.84×10^{-3} respectively. The ratios of activity product to solubility product constant at 38.34°C for $CaSO_3 \cdot \frac{1}{2}H_2O$ and $CaSO_4 \cdot 2H_2O$ are 10.6 and 1.79 respectively. This shows that the solution is highly supersaturated with respect to $CaSO_3 \cdot \frac{1}{2}H_2O$ and moderately supersaturated with respect to $CaSO_4 \cdot 2H_2O$. These numbers will be of value in conjunction with scaling studies to define scaling tendency.

TABLE 12 - DISTRIBUTION ACTIVITIES OF KEY SPECIES

(See Table 10 - Scrubber Effluent)

```
10 JUN 71    14:41:57.533                                     TEMPERATURE    38.340  DEG. C
                               INPUT MOLES

 SO2  =1.00000-02
 CO2  =3.07000-03
 SO3  =3.34000-02    N2O5 =1.75000-03    CAO  =3.77000-02    MGO  =1.24000-02
 NA2O =3.85000-04    HCL  =9.00000-03    H2O  =5.55084+01


                         AQUEOUS SOLUTION EQUILIBRIA

          COMPONENT          MOLALITY            ACTIVITY        ACTIVITY COEFFICIENT
          H2O                                                       9.987-01
          H+                 7.830-06            6.174-06           7.887-01
          OH-                1.327-08            1.022-08           7.708-01
          HSO3-              5.755-03            4.175-03           7.253-01
          SO3--              3.740-04            1.270-04           3.400-01
          SO4--              1.335-02            4.035-03           3.017-01
          HCO3-              7.014-04            5.401-04           7.703-01
          CO3--              4.395-08            1.471-08           3.346-01
          NO3-               3.477-03            2.403-03           7.036-01
          HSO4-              2.325-06            1.793-06           7.708-01
          H2SO3              1.107-05            1.127-05           1.019+00
          H2CO3              7.247-03            7.371-03           1.019+00
          CA++               1.935-02            7.549-03           3.915-01
          CAOH+              2.935-09            2.263-09           7.703-01
          CASO3              2.564-03            2.614-03           1.019+00
          CACO3              1.374-07            1.397-07           1.019+00
          CAHCO3+            1.017-04            7.833-05           7.703-01
          CASO4              9.970-03            1.016-02           1.019+00
          CANO3+             7.054-05            5.437-05           7.708-01
          MG++               9.064-03            3.203-03           3.533-01
          MGOH+              2.071-09            1.595-09           7.703-01
          MGSO3              3.253-04            3.315-04           1.019+00
          MGHCO3+            1.894-05            1.461-05           7.708-01
          MGSO4              4.071-03            4.148-03           1.019+00
          MGCO3              1.011-07            1.030-07           1.019+00
          NA+                7.440-04            5.756-04           7.737-01
          NAOH               1.300-12            1.325-12           1.019+00
          NACO3-             2.290-10            1.765-10           7.708-01
          NAHCO3             1.758-07            1.791-07           1.019+00
          NASO4-             2.512-05            1.937-05
```

TABLE 12 - DISTRIBUTION OF KEY SPECIES

```
              NANO3             5.436-07            5.591-07            1.019+00
               CL-              9.390-03            7.551-03            7.381-01
 PSO2 =1.46130-06  ATM.
 PCO2 =9.37717-02  ATM.

                              MOLECULAR WATER = 9.99975-01 KGS.

    SPECIFIED PH =       5.670         IONIC STRENGTH = 1.08977-01           RES. E.N. =  -2.692-0
```

Another number of importance for engineering calculations is the partial pressure of SO_2. From Table 12 it is seen that P_{SO_2} in the scrubber effluent is 1.46×10^{-6} atm or about 1.5 ppm. This is a necessary input for SO_2 vapor-liquid mass transfer calculations. In similar fashion other activities will be required for solid-liquid mass transfer rates.

ACKNOWLEDGEMENTS

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ON-STREAM CHARACTERIZATION OF THE LIMESTONE/DOLOMITE WET SCRUBBER PROCESS

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ABSTRACT

The development of control methodology for sulfur oxide and particulates from power plant emissions by wet scrubbing requires accurate and reliable measurements of process variables. Planned OAP process demonstration studies will result in a requirement for a large number of chemical analyses requiring 1) automatic instrumental methods and 2) associated data acquisition and processing capabilities which exceed current instrumental capabilities. This paper describes activities undertaken at TRW Systems under Contract 68-02-0007 toward the development of methods suitable for optimization and control of the wet limestone and dolomite scrubbing processes by continuous onstream analytical methods. Emphasis was placed on development of continuous on-line methods for slurry sampling and separation that do not disturb the chemical steady state condition. Establishment of sampling requirements and an effective means for total phase separation in a period less than thirty seconds were accomplished.

Analytical instrumental methods having capability of continuous or slug flow analysis within two minutes were identified for characterization of the separated solid matter and liquor. Analytical methods were identified which permit continuous X-ray analyses of solid constituents for sulfur, calcium, magnesium and iron contents. Liquid phase analyses methods were established for instrumental analysis of acidity, sulfite, sulfate, calcium, magnesium and carbonate contents. A new method for rapid analysis of sulfite content based on furfural bleaching is being carried to a state of prototype analytical instrument development. In addition, approaches for total complete on-line analysis of other wet limestone scrubber constituents have been identified.

INTRODUCTION

The development of control methodology for sulfur oxide and particulates from power plant emissions by limestone/dolomite wet scrubbing requires accurate and reliable measurements of process variables. Efficient, proven methods for many of these measurements have not yet been developed. The monitoring of the complex chemistry involved in this scrubbing process and associated sampling of representative samples in quiescent and dynamic mixtures of liquors, slurry and solids are in themselves challenging analytical problems. In addition, planned OAP process demonstration studies will result in a requirement for a large number of chemical analyses requiring 1) automatic instrumental methods and 2) associated data acquisition and processing capabilities which exceed current instrumental capabilities.

The chemistry of the process is not sufficiently understood at the present time because of the lack of definitive mass balance information involving the chemical species existing in the scrubbing solution. The development of suitable on-stream analysis methods will provide a means to fill this gap through detailed characterization of the process. High analytical accuracy is not a requisite of the needed methods but rather they must be adaptable to instrumental techniques that will be reliable, reproducible, cost effective and employ hardware requiring little maintenance. This paper describes activities undertaken at TRW Systems under Contract 68-02-0007 for development of methods suitable for optimization and control of the wet limestone/dolomite scrubbing processing by continuous on-stream analytical methods.

SAMPLING AND ANALYSIS REQUIREMENTS

As described in earlier papers presented at this symposium, the potential chemical species in limestone/dolomite wet scrubbing processes are numerous. Table I lists the major and minor species that could be present in the limestone/dolomite wet scrubber slurry. The number of chemical variables studied were limited to only the key parameters affecting the operation of the limestone/dolomite scrubber in order to scope the present program at a manageable size. As a result, activities were focused on establishing instrumental criteria and identification of instruments suitable for on-line monitoring of the following chemical species or characteristics:

TABLE I

POSSIBLE LIMESTONE/DOLOMITE SLURRY COMPONENT DISTRIBUTION[a]

Major Components		Minor Components	
Liquid Phase	Solid Phase	Liquid Phase	Solid Phase
Ca^{2+}	CaO	K^+	MPO_4
Mg^{2+}	MgO	$PO_4^{\equiv}$	SiO_2
HSO_3^-	$Ca(OH)_2$	NO_3^-	CaF_2
SO_4^{2-}	$Mg(OH)_2$	Na^+	PbS
HCO_3^-	$CaSO_3$	Fe^{3+}	Al_2O_3
SO_3^{2-}	$CaSO_4$	Fe^{2+}	S_8
CO_3^{2-}	$CaCO_3$	Mn^{2+}	ZnS
	$MgCO_3$	Cl^-	Na_2O
		NO_2^-	MSO_4
		NO_3^-	FeS_2
			Fe_2O_3
			TiO_2
			CO_2O_3

[a] Distribution of components is dependent on pH and temperature.

- Calcium ion concentration
- Magnesium ion concentration
- Sulfite ion concentration
- Sulfate ion concentration
- Carbonate ion concentration
- pH
- Ionic strength

The analysis methods were selected for evaluation based on their applicability for characterizing slurries, filtered solutions and dry and/or separated solids on a continuous basis.

On review of the scrubbing process variables several sampling requirements were identified relating to characterization of the scrubbers mixture. These sampling requirements are shown in Table II. During a literature review phase, sampling, separation and quenching of reactants were identified as major problem areas that had to be resolved prior to application of any analytical techniques to on-stream analysis. A system capable of handling

TABLE II

LIMESTONE SLURRY SAMPLING REQUIREMENTS

- Slurry Solids Content - 0 to 15% w/w
- Slurry Sample Quantity - $\leq$1% of stream flow
- Instream Sampling Rate - <2X stream velocity
- Phase Separation
  - 100% removal of >0.5μ particles in liquid
  - Lag Time - <30 seconds
- Sampling Rate - 30 samples/hr, min
- Analysis Time - 2 min, max.
- Easily Maintained

a sampling rate of 30 samples per hour necessitated the use of a rapid separation of slurry and isolation of solid and liquid phases and was a key milestone prior to developing analytical techniques. The sampling rate was established assuming specific combinations of scrubber designs and analysis location and sample frequency. An example which fulfills this requirement is three different scrubber design processes sampled every 30 minutes at five different locations. Variations of sampling locations up to eight and sampling frequency of up to 15 minutes cover a wide range of samples to be analyzed. For the purpose of establishing the ability of an instrument to meet the continuous on-loop analysis requirements a total of 30 samples per hour was taken as a nominal value.

The sampling requirements, process characteristics and the need for rapid analysis established the instrument requirements identified in Table III. During the early phases of the program, analysis error requirements for the key chemical constituents present in the limestone/dolomite scrubber were based on estimates provided by the OAP Project Monitor of concentration range and relative error of the methods required for 20% sulfur mass balance closure as determined by the Bechtel Corporation. These data are presented in Table IV and were used to guide the direction of the program pending updating of these requirements in concurrent programs by the Radian Corporation and Bechtel Corporation. It is interesting to compare the cost associated with analyzing this number of samples by alternative

TABLE III

INSTRUMENT REQUIREMENTS

- Selective Ca^{++}, Mg^{++}, H^{+}, $SO_3^{=}$, $SO_4^{=}$
- Continuous or plug flow analysis
- Minimum analytical lag time
- Facile calibration
- Routine operation
- Rugged construction
- Low maintenance
- Acceptable accuracy

TABLE IV

LIQUID ANALYSIS REQUIREMENTS

	Concentration Range mM	Maximum Allowable Relative Error*
Mg^{++}	1 - 1000	3
Ca^{++}	1 - 250	3
$SO_3^{=}$	1 - 150	3
$SO_4^{=}$	1 - 500	15
$CO_3^{=}$	1 - 20	15
Na^{+}	1 - 500	15
K^{+}	1 - 500	15
Cl^{-}	1 - 500	15

*For 20% sulfur mass balance closure

laboratory procedures as opposed to on-line instrumentation. Table V lists the estimated labor for laboratory analyses of sulfite, calcium, magnesium, sulfate and pH and solids analysis for calcium, total sulfur and magnesium. The labor hours per sample are estimated to be between 2.1 and 5.2 hours. The extrapolation of these values to an hour, daily, and monthly basis show that a large amount of labor is required for minimum characterization of a limestone/dolomite scrubber. When the cost of this labor is

TABLE V
ESTIMATED LABOR FOR LABORATORY ANALYSES

	Minimum	Maximum
Liquid Analyses		
Sampling, Hours	0.1	0.1
$SO_3^=$, (Titr), hrs	0.2	0.5
Ca^{++}, (AA) Hours	0.2	0.3
Mg^{++}, (AA) Hours	0.2	0.3
$SO_4^=$, (Grav) Hours	0.7	3.0
pH, Hours	0.1	0.1
Solids Analyses		
Ca S (X-ray) Hours Mg	0.6	0.9
Total Labor Manhours/Sample	2.1	5.2
For 30 samples/hour, manhours	63	156
Per 8-hour day, manhours	504	1,248
Per 30 days, manhours	15,120	37,440

projected together with its necessary supervision, the use of automated on-line analyses is readily justified on a cost saving basis alone without consideration of advantages of reproducible sampling, calibration and sample representation.

SLURRY SAMPLING AND SEPARATION

During the course of this program several vendors were contacted to determine whether they had equipment available which could separate a limestone/dolomite slurry meeting the following operating parameters:

- Flow rate - to 300 lb/minute (a portion of this flow could be diverted prior to the separator)
- Solids, % - 0.5 - 15
- Particle size, micron - 5 - 300
- Density of solids (unpulverized) g/ml - 2.7 - 2.9
- Density of liquid, g/ml - 1.005 - 1.080

- Temperature, °F - to 150
- System to exclude air durirg and after separation - both phases
- Time to effective separation - 15 seconds

Ten companies replied positively that they had equipment which might fit these operating parameters. The separation principles identified included continuous discharge centrifuges, in-line filter cartridges, belt filters, and a continuous cyclone cone centrifuge. Laboratory evaluation of these principles was undertaken using spent slurry obtained from the Key West Electric Company and equipment sold by deLaval, Sharples and Demco. A summary of the findings are shown in Table VI. It was found that neither the cone centrifuge nor a combination of the solid bowl centrifuge-centrifugal cone provided clear-cut separation as indicated by slight cloudiness in the discharge fluids. An optically clear fluid would demonstrate excellent solids rejection and is needed for any subsequent colorimetric

TABLE VI

SUMMARY OF LABORATORY EVALUATION OF SEPARATION METHODS

- Continuous centrifugation - deLaval Laboratory Gyro-tester

  Performance - 30 sec. operation at 0.5 gpm feed - 3% Zurn slurry

  Results - very nearly clogged
- Cone centrifuge (cyclone) - Demco 18mm cone

  Performance - continuous - pretreatment device

  Results - very promising
- Solid bowl centrifuge/cone-Sharples solid bowl/Demco

  Performance - minimum one hour continuous operation

  Results - slight turbidity
- Polishing filter - Accu-flow in-line convoluted cartridge

  Performance - high capacity - quick interchange

  Results - optically clear output

characterization of the liquid phase. However, inclusion of a polishing filter, such as an Accu-Flow in-line convoluted cartridge filter downstream resulted in a high capacity unit providing continuous transparent liquid for periods as long as several hours depending on the initial solid loading.

The cyclone cone separator was fabricated by Demco to meet TRW's design requirements and is shown schematically in Figure 1. The device consists of an 18-mm cone fabricated from 316 stainless steel and possesses an adjustable orifice control. The unit operates with a 35 psi minimum pressure differential with an inlet feed velocity of 46 ft/second and a volume demand of 1 gpm. Throttling the underflow to cause an overflow to underflow ratio of 45, resulted in an overflow to underflow solids content ratio of 0.0204. Consequently, operation of the Demco in this mode permitted rejection of approximately 98% of the original solids content. The solution containing 2% of the original solids is readily handled through banked parallel polishing filters to provide optically clear liquid. The life time of the filters are at least one hour and use of a parallel bank system permits back flushing to reactivate a spent filter when it is isolated from the flow loop.

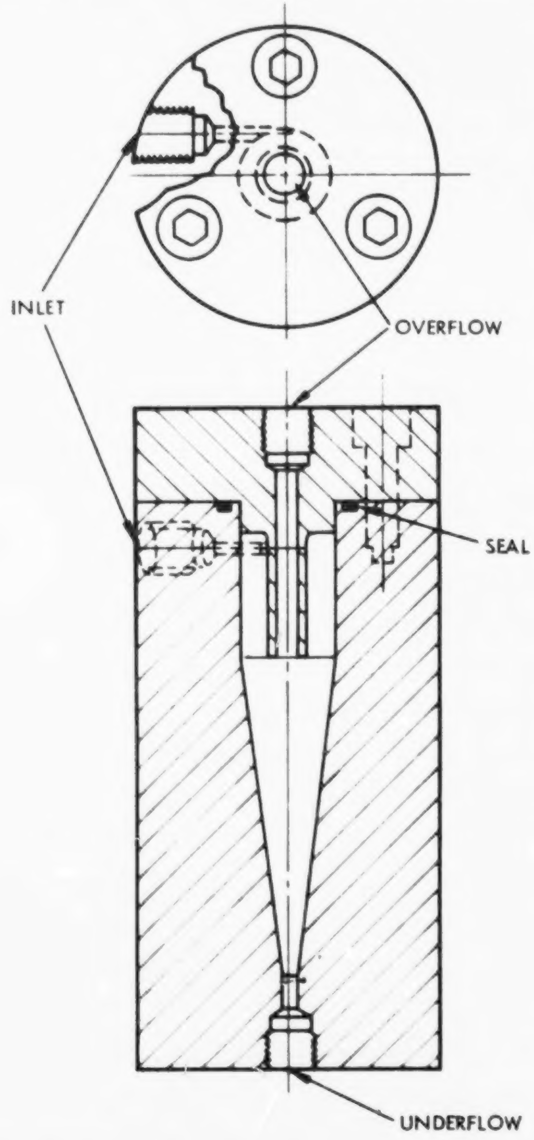
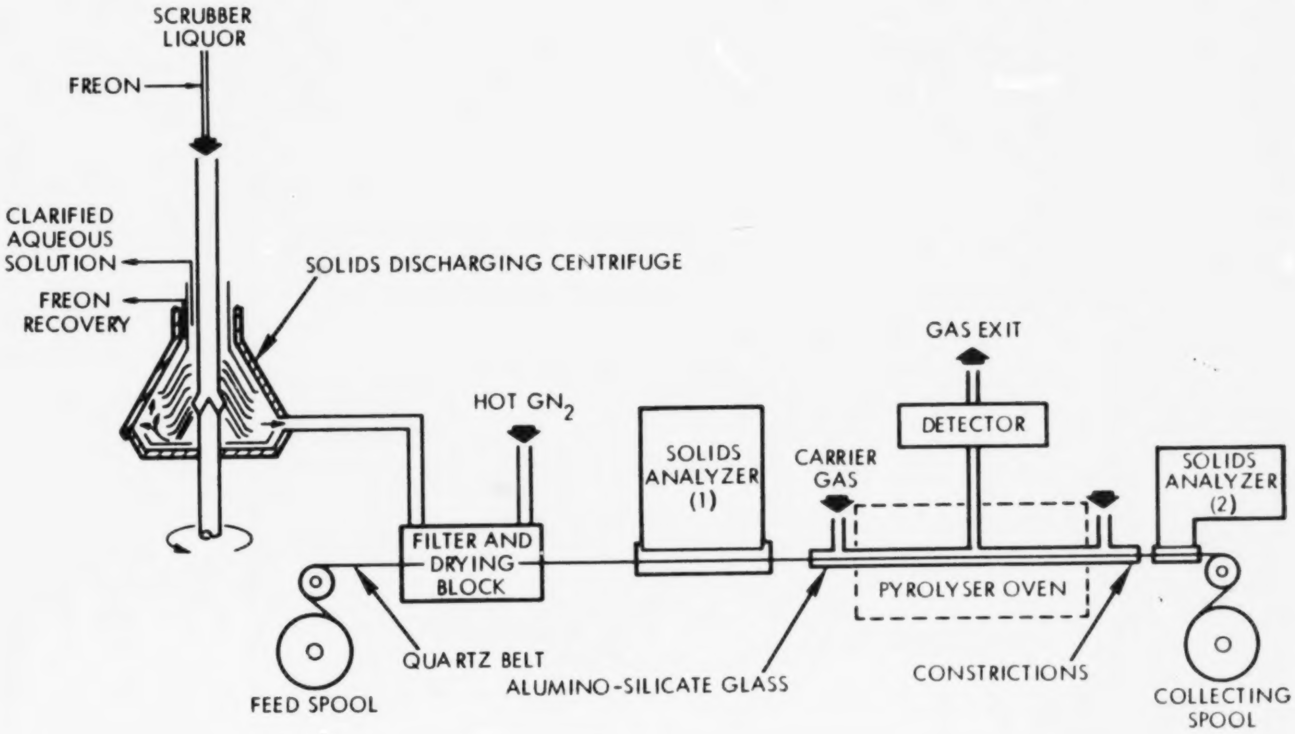


Figure 2. DEMCO Centrifugal Separator

A continuous stage separation concept has been devised which is capable of achieving "instantaneous quenching of reaction" within an arbitrary allotted time of 15 seconds in such a manner as to present "dry" stream of slurry solids for continuous analysis. In the conceptual design shown in Figure 2, the first stage utilizes a liquid/liquid/solid centrifugal separator, such as one of the deLaval PX solids ejecting centrifuges. The separator would be fed by the slurry stream, from the point in the scrubber process under scrutiny. A second heavy liquid phase such as a Freon, trichlorethylene or other heavy inert solvent would be added to the slurry as it entered the separator. As shown in the schematic drawing, the light, clear aqueous phase is separated from an annular zone near the center, the denser non-aqueous phase is ejected from an intermediate zone while the solids, essentially free from aqueous liquid contamination are continuously discharged from the outermost zone and transferred to the quartz filter carrier belt. In the filter/drying housing, which is the second stage, residual inert solvent is volatilized in a heated high pressure dry nitrogen stream before the solids pass into the solids analyzer.

ANALYSIS METHODS

During the course of this program many alternative instrumental methods were considered as candidates for adaptation to continuous on-line analysis. The details of these evaluations will be documented in the final report to Contract 68-02-0007. A summary of our recommendations is provided in Table VII which identifies methods of analysis for liquid phase and solid phase components. The applicability of the recommended methods have been confirmed through analysis of known simulated slurry mixtures and actual slurry mixtures and constituents obtained from operating wet limestone scrubbing units at the Key West Electric Company, Kansas Power and Light Company and Shawnee Power Plant. As can be seen from Table VII, considerable use is made of X-ray and atomic absorption methods which handle samples with minimum pretreatment. Colorimetric methods have been recommended for sulfur (IV) content in solution and tentatively for nitrite and nitrate. The turbidimetric method for dissolved sulfate is a standard method which requires the addition of barium salts after acidification and heating to remove carbonate and bisulfite interferences. Brief discussions are provided below on the continuous X-ray analysis methodology and the colorimetric dissolved sulfur (IV) analysis method. This information is provided because of the special consideration and testing that were required to ensure acceptable results for analysis in a limestone slurry environment. The other methods



SCHEMATIC DESIGN OF CONTINUOUS SOLID SEPARATION AND ANALYSIS APPARATUS CONCEPT

Figure 2. Schematic Design of Continuous Solid Separation and Analysis Apparatus Concept

TABLE VII
RECOMMENDED METHODS FOR ON-LINE ANALYSIS OF LIQUID AND SOLID PHASE WET SCRUBBER COMPONENTS

Liquid Phase	
• S (IV) ($HSO_3^- + SO_3^=$)	Colorimetric (Furfural Bleaching)
• Ca^{++}	Atomic Absorption
• Mg^{++}	Atomic Absorption
• $Fe^{++} + Fe^{+++}$	Atomic Absorption
• K^+	Atomic Absorption
• Na^+	Atomic Absorption
• Total Solids	Conductivity
• pH	Electrometry
• $CO_3^=$	Acidification, Heat + IR Determination of Evolved Gas
• $SO_4^=$	Acidification, Heat and Turbidimetric
• Total Sulfur	X-ray (limit 9.4 *mM*)
• NO_2^-	Colorimetric* (Brucine)
• NO_3^-	Colorimetric* (Brucine)
Solid Phase	
• Total Sulfur	X-ray
• Ca	X-ray
• Mg	X-ray
• Fe	X-ray
• Si	X-ray
• Al	X-ray
• SO_2, CO_2	Pyrolysis + IR Determination*

*Tentative projected method

are relatively straightforward and are considered routine by those experienced in process control analysis and monitoring.

X-RAY ANALYSIS EQUIPMENT

Commercially available analysis equipment was evaluated with the identification of the Applied Research Laboratories (ARL) process control X-ray quantometer (PCXQ) as being suited for continuous on-line analysis of selected species for both liquid, solid or slurry phases. This instrument was evaluated for applicability of analysis of these mixtures by determination of synthesized simulated mixtures. The equipment can be obtained with a slurry presenter and can handle up to 15 slurry streams sequentially in an automative mode for elements from magnesium upwards in the periodic table. Nine spectrometric channels of information are available and nine elements in a slurry stream can be simultaneously detected and analyzed. A bulk density monitor is incorporated into the system along with a fixed external standard.

In the ARL unit the limit of detection for sulfur is 0.03%. The sensitivity of sulfur for on-line slurry units utilizing helium X-ray path and a Kapton cell window was determined to be significantly less than the 0.25% absolute value considered to be the lowest reasonable value likely to be encountered in the slurry mixture. This detection limit corresponds to a sulfur content of 9.4 *mM* in the liquid phase. Consequently, X-ray cannot be used for determining dissolved sulfate and sulfite concentrations which total less than 9.4 *mM*. The determined repeatability of the unit was 0.4% relative, far less than the 3% which has been viewed as a requirement.

As expected, the key for obtaining good X-ray information is to establish elemental calibration curves using comparable matrix materials which will be present in the analysis sample. This requires incorporation of both limestone and flyash to ensure comparable matrices. The effect of particle size on analytical accuracy is most striking when the size if greater than 40 microns. However, the case of spent limestone/flyash solids, approximately 90%, have a particle size below 30 microns. For the solids analyzed from Key West Electric Company, Shawnee Power Plant and Kansas Power and Light Company, more than 95% of the particles were less than 40 microns. Consequently, the variability that can be introduced by particle size will not play a significant role in the analysis of these mixtures.

Comparison of the on-line analysis capability of the ARL unit with representative laboratory analysis X-ray equipment shows that considerably more analyses can be accomplished using the ARL PCXQ as is seen in Table VIII. Extrapolation of these data to obtain operating costs show the ARL unit has a 4.5-fold advantage over the best competitor per analysis ($1.33 vs $6.00) and a 3.4-fold cost per element analyzed advantage (18¢ vs. 62¢).

TABLE VIII

ELEMENTAL ANALYSIS CAPABILITIES OF CANDIDATE X-RAY UNITS

X-Ray Unit	Estimated Maximum Number of Analyses Per 8-hour Shift	Number of Elements Per Analysis	Total Elemental Analyses
A.R.L. (on-line)	240[a]	8	∿1800
A.R.L. (lab)	160[a]	7	∿1000
G.E. (lab)	160[a]	1	∿ 160
Kevex (lab)	45[b]	∿50 (16)	∿ 640

[a] Two-minute residence period in spectrometer

[b] Ten-minute residence period in spectrometer

DETERMINATION OF DISSOLVED SULFUR DIOXIDE

During the review of candidate analytical methods for the determination of dissolved sulfur dioxide (HSO_3^- and $SO_3^=$) it was determined that no satisfactory methods existed for determining concentrations in the range to be found in the limestone slurry mixture (see Table IV). Consequently, a new method based on bisulfite bleaching of the furfural UV absorption was developed to facilitate this analysis. This method is based on the chemical equation b in Equations 1 - 4 and depends on the bleaching of the 276 *nM* absorption of furfural by reaction with bisulfite.

$$C_4H_3OCHO + HSO_3^- \rightleftarrows C_4H_3OCHOHSO_3^- \qquad (1)$$

$$C_4H_3OCHOHSO_3H \rightleftarrows C_4H_3OCHOHSO_3^- + H^+ \qquad (2)$$

$$H_2SO_3 \rightleftarrows H^+ + HSO_3^- \qquad (3)$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^= \qquad (4)$$

The absorbance, A, at 276 *nM* is directly related only to the amount of furfural in solution when the pH of the media is maintained around 4.0 in accordance with the Lambert-Beer-Bouguer Law.

$$A = abc_F \qquad (5)$$

where a = molar absorptivity of furfural
b = optical path length
c_F = concentration of uncombined furfural

The equation of the bleaching reaction (Equation 1) is governed by the formation constant, K

$$K = \frac{c_A}{c_F[HSO_3^-]} \tag{6}$$

where c_A = concentration of furfural-sulfite adduct
$(c_A = c_o - c_F)$
$[HSO_3^-]$ = concentration of uncombined bisulfite

Combining Equations 5 and 6 results in a relationship of absorbance and bisulfite ion as shown in Equation 7.

$$\frac{1}{A} = \frac{K}{abc_o} [HSO_3^-] + \frac{1}{abc_o} \tag{7}$$

It is interesting to note that this method was first developed for the determination of furfural and prior to this study has not been used for the determination of bisulfite. The reason for this is because in most situations colorimetric procedures are used for determining low concentrations of chemical species but in the limestone scrubber case the concentration of bisulfite (1 - 150 *mM*) is too large for trace analysis methods (without massive dilution) and not readily adaptable to common macro titrimetric procedures (without using large volumes and dilute titrants).

Detailed studies of the effect of pH, diverse ions, temperature, and time to constant color development has resulted in the selection of a single reagent addition consisting of furfural, phosphate buffer and sulfamic acid (to remove trace concentrations of nitrite interference). The reproducibility of the method has been determined to be better than 2% relative or 0.2*mM* absolute whichever is higher. This method is currently being adapted to a plug flow analyzer system.

LABORATORY BENCH SCALE SCRUBBER

A basic modular designed bench scale test loop wet scrubber (see Figure 3) was fabricated to permit evaluation of the recommended methods under simulated use conditions. A loop system was selected because of the necessity of: 1) closely approximating the full scale operating unit, 2) accurate control, and 3) producing stable (equilibrium) and unstable

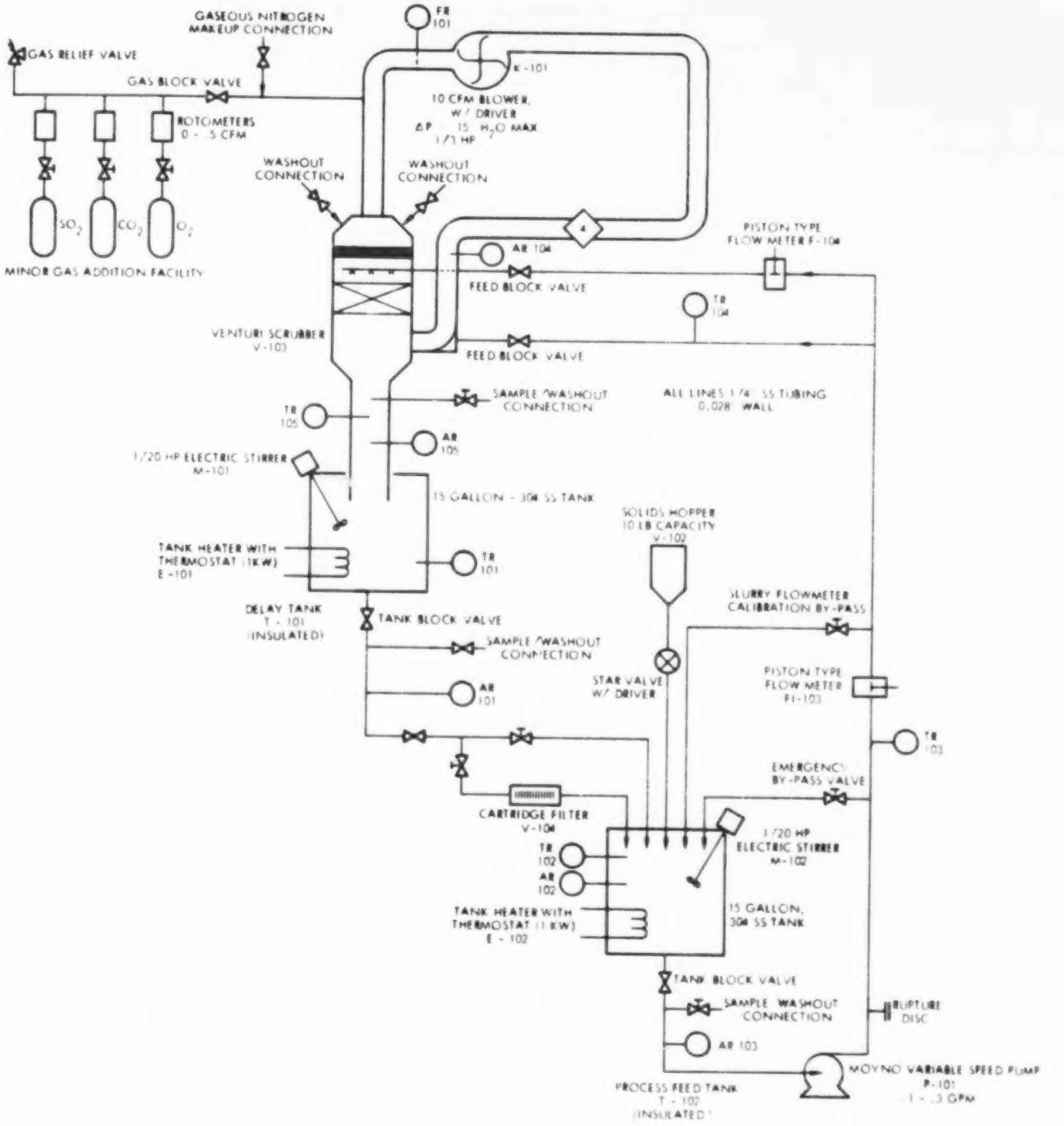

GASEOUS NITROGEN MAKEUP CONNECTION
GAS RELIEF VALVE
GAS BLOCK VALVE
ROTOMETERS 0 - .5 CFM
SO_2
CO_2
O_2
MINOR GAS ADDITION FACILITY
FR 101
K-101
10 CFM BLOWER, W/ DRIVER ΔP .15" H_2O MAX 1/3 HP
WASHOUT CONNECTION
WASHOUT CONNECTION
4
AR 104
FEED BLOCK VALVE
PISTON TYPE FLOW METER F-104
TR 104
VENTURI SCRUBBER V-103
FEED BLOCK VALVE
SAMPLE /WASHOUT CONNECTION
ALL LINES 1/4" SS TUBING 0.028" WALL
TR 105
AR 105
1/20 HP ELECTRIC STIRRER M-101
15 GALLON - 304 SS TANK
TANK HEATER WITH THERMOSTAT (1KW) E-101
TR 101
SOLIDS HOPPER 10 LB CAPACITY V-102
DELAY TANK T - 101 (INSULATED)
TANK BLOCK VALVE
SLURRY FLOWMETER CALIBRATION BY-PASS
SAMPLE /WASHOUT CONNECTION
STAR VALVE W/ DRIVER
PISTON TYPE FLOW METER FI-103
AR 101
TR 103
EMERGENCY BY-PASS VALVE
CARTRIDGE FILTER V-104
1/20 HP ELECTRIC STIRRER M-102
TR 102
AR 102
TANK HEATER WITH THERMOSTAT (1 KW) E - 102
15 GALLON, 304 SS TANK
TANK BLOCK VALVE
SAMPLE WASHOUT CONNECTION
RUPTURE DISC
AR 103
MOYNO VARIABLE SPEED PUMP P-101 .1 - .3 GPM
PROCESS FEED TANK T - 102 (INSULATED)

Figure 3. Bench Scale Scrubber Analysis Loop

(non-equilibrium) conditions for evaluating candidate instruments under known, controllable conditions with realistic compositions.

The system consists of a bench scale Venturi scrubber with a second stage packed bed, fitted with a recirculating gas stream. The pressure drop associated with the packed bed is about 0.5-inch of water, the pressure drop due to the Venturi is about 1-inch of water and the pressure drop associated with the ducting is 0.4-inch of water. The packed bed is 9-inch deep and has a diameter of 4-inch. The ducting is 2-inch I.D. throughout. The Venturi has a throat size of 1-inch.

The recirculating gas stream is moved via blower K-101. The composition of the recirculating gas stream is controlled by the Minor Gas Addition facility. This facility allows the addition of small amounts of gases via rotometers and bottled gas. Gases such as SO_2, CO_2 and O_2 are controlled in this manner. Nitrogen is occasionally bled into the system to make up that amount which has been absorbed by the circulating slurry. The level of slurry in the liquid separator V-103 is controlled in this manner. The composition of the gas stream is monitored by gas analyzer AR-104, which gives compositions of SO_2, CO_2 and O_2 in the circulating stream. Flow of the gas stream is given by a differential pressure cell, FR-101.

The liquid slurry exits the Venturi scrubber via the liquid separator V-101. The temperature in the downcomer is measured and recorded by TR-105. Analyses of the slurry is also provided in the downcomer by analyzer AR-105 (type of instrument to be determined during Contract 68-020-0007. The liquid stream from the liquid separator dumps into a 15-gallon delay tank, T-101, where it is agitated with a 1/20 horsepower electric laboratory stirrer (M-101) and the temperature is adjusted and controlled by a tank heater E-101. The temperature is measured and recorded by TR-101. The residence time in this delay tank is about one hour with a design slurry flow of 0.2 gpm.

The liquid slurry travels to the process feed tank along one of two routes. It can travel along the straight transfer section, or it can be diverted through a filter. The purpose of the filter is to take out solids from the circulating slurry. The composition of the slurry exiting the delay tank is monitored and recorded by AR-101.

The solids content of the slurry in Process Feed Tank (T-102), a 15-gallon, 304 stainless steel tank equipped with a 1/2 horsepower laboratory stirrer, is adjusted by adding limestone from the solids hopper via a star valve. The composition of the tank is monitored and recorded by the process analyzer AR-102. The temperature in this tank is maintained by tank heater E-102 and is measured and recorded by TR-102.

The adjusted slurry from T-102 is transported along the transfer line with a positive displacement pump, P-101. This pump has the capacity of 0.1 to 0.3 gpm. This range is required so that the liquid to gas ratio present in the packed bed Venturi scrubber is capable of being changed. The characteristics of this stream are given in Table VII. Accurate flow of the pump output is adjusted via the recycle stream to T-102. The flow is monitored and recorded on FI-103 which receives a signal from a positive displacement piston type flow meter. The temperature in this section of line is recorded on TR-103. The flow then splits, part going through a counter-current flow section packed with 1/4-inch Raschig rings. The other part of the flow goes to the throat of the Venturi. The flow which goes to the packed section is measured and recorded on a flow indicator FI-104, which receives its signal from a positive displacement flow meter.

All liquid lines present in the bench loop simulator are of 1/4-inch polypropylene, with an .028-inch wall. Utilizing this type of tubing, the flow velocity will be about 1.8-feet per second.

This unit has been used to test the applicability of the recommended methods under controlled conditions. These current studies have confirmed the fact that 1) the constituents of flyash catalyze the oxidation of sulfite to sulfate and 2) the presence of dissolved oxygen in the slurry (although only 0.5 *mM* at 125°F) contributes significantly to sulfite oxidation.

SUMMARY

Methods have been identified which are suitable for rapid sampling and on-line chemical analysis of the principle constituents limestone/dolomite wet scrubber solutions. Utilization of the identified methods in process demonstrations will permit rapid chemical changes in the scrubber slurry as a function of process variables and provide needed basic information for subsequent process optimization.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of J. Craig (Zurn Engineering), Lee Bruton (Kansas Power and Light Company), Jim Martin (Combustion Engineering), and Joe Barkley (Tennessee Valley Authority) for their cooperation and assistance in acquisition of limestone scrubber slurry and solid samples as well as Bob Statnick, OAP Project Monitor for his guidance and encouragement. In addition, the authors wish to acknowledge members of the TRW Systems Chemistry and Chemical Engineering Laboratory for their efforts on this program.

PARTICULATE EMISSIONS FROM TWO LIMESTONE WET SCRUBBER

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PARTICULATE EMISSIONS FROM TWO LIMESTONE WET SCRUBBERS

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Abstract

During field tests on a full-scale flooded bed scrubber and a pilot plant scrubber, data were collected on the variation in mass emission levels and the size distribution and chemical composition of the particle emissions.

A filter sample and three runs with an Andersen stack sampler were taken at the outlet of the flooded bed scrubber. We found that half of the mass emissions from this scrubber are smaller than 1.6 μm in diameter. Using electron diffraction, we determined that 70% of these emissions are hydrated crystals of calcium sulfate.

Filter samples taken from the pilot plant scrubber showed that the particles emitted from this scrubber are even smaller than those from the flooded bed scrubber: The mass average diameter is 0.8 μm. Here, again, a large majority of the particle is calcium sulfate.

The size, shape and quantity of small calcium sulfate crystals indicate that much of the emissions from limestone wet scrubbers are being produced by the evaporation of fine droplets containing dissolved solids.

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* Presented by Ronald G. Draftz

Introduction

During our program (1) to evaluate particulate sampling methods for wet scrubbers, field tests were conducted on a full-scale flooded bed scrubber at Kansas Power and Light (KPL) Lawrence, Kansas, and the Zurn pilot plant Dustraxtor® scrubber at TVA's Shawnee plant. Both scrubbers were operating on coal-fired power plants.

Although our primary task was to evaluate the effectiveness of various methods of determining particle mass concentration and size distribution, in the outlet and inlet of wet scrubbers, we were also interested in obtaining some data on the composition and size distribution of the particulate in the scrubber outlet. We did not attempt to determine the exact mass loading from either unit.

Sampling Methods

With the exception of the particulate collection device and the diameter of the sampling probe, all samples were collected using a standard EPA sampling train (2). A summary of the sampling conditions of the various particulate collectors is shown in Table 1.

TABLE 1

Summary of Sampling Conditions

Conditions	KPL Flooded-bed scrubber outlet				Zurn pilot scrubber outlet
particulate collector	filter	Andersen stack sampler			cyclone + filter
sampling time (min)	30	1	4	10	45
flow rate (SCFM)	3.68	1.0	1.25	1.25	1.07
collector temperature (°R)	—	760	760	760	695
probe diameter (in.)	3/8	1/4	1/4	1/4	1/4

Tests at the outlet of the flooded-bed scrubber included collecting particles with glass-fiber filters, an improved Andersen Stack Sampler, and a 7-stage cascade impactor. The Andersen Stack Sampler tests were designed to evaluate particle re-entrainment using three sampling times, 1, 4, and 10 minutes. An experimental cascaded cyclone and high-temperature membrane filter were used for sampling the outlet of the Zurn scrubber.

None of the samples were collected under isokinetic conditions because the particulate matter encountered in these tests is so small that particle size bias was assumed to be negligible. Since the samples were collected from only one point they are not completely representative of the stack emissions. However, the samples from KPL were taken 24 inches inside one stack, and the velocity profile was very flat, leading us to believe that the particulate was evenly distributed. The outlet of the Zurn scrubber is only 8 in. in diameter so that fixed point sampling should be representative.

Analysis Methods

Particulate collected on the glass-fiber filter at the flooded bed scrubber was sized using an optical microscope in conjunction with a Millipore IIMC automatic image analyzer, set to measure Feret's diameter Transmitted light illumination was used with a 100X oil-immersion objective on the microscope. Five samples of particulate were removed from different locations on the filter and mounted in glycerol on glass slides. Glycerol was chosen because its refractive index is significantly different from those of the major components found in the samples, calcium sulfate and glass spheres. A total of 2,919 particles were counted in 10 size intervals from 0.2 μm to 4.5 μm. Number fractions in each interval were converted to mass fractions using the cube of the geometric mean of the interval.

The size distributions of the particles collected by the Andersen Stack Sampler were obtained by first determining the fraction of the total mass collected on each stage. The particulate collected on each plate was weighed to the nearest 0.01 milligrams using a semi-micro analytical balance. The characteristic cut-off point, d_{50}, for each stage was calculated using the data supplied by 2000, Inc., for operating conditions of 760° R and a particle density of 2.5 g/cm^3 (3). The cumulative distribution was produced by plotting the d_{50} for each stage, against the sum of the fractions collected below that stage. More precise methods for determining size distributions have been reported which take into account the variation of d_{50} with the size distribution (4, 5). However, for our purpose, such precision was unnecessary.

The particles collected by the experimental cascaded cyclone and filter were sized with a different method because of the extremely small size of the particle sampled. Particles from several samples removed from the cyclone and filter were photographed at magnifications of 10,000X and 5,000X repsectively, with a Cambridge Stereoscan IIA scanning electron microscope (SEM). The particles were then sized using an epidiascope attachment to the IIMC automatic image analyzer. Again Feret's diameter was used and weight fractions were obtained in the manner described above.

The fractional efficiency curve was obtained from the fractional mass distributions of the cyclone and filter catch. The mass collection efficiency of the cyclone is defined as:

$$K = \frac{Mi - Mo}{Mi} = \frac{(Mc + Mo) - Mo}{Mc + Mo}$$

where Mi, Mc, and Mo are the inlet mass, mass of the cyclone catch, and outlet mass respectively.

It is easy to show that the fractional collection efficiency of size X is given by

$$E_x = \frac{C_x}{C_x + \frac{F_x (1 - K)}{K}}$$

where C_x and F_x are the mass fractions at size X in the cyclone catch and outlet or filter catch.

Extensive electron diffraction analysis of individual particles from the filter sample from the flooded-bed scrubber was performed using an RCA EMU 4 transmission electron microscope and later confirmed for the total sample using x-ray diffraction analysis. Elemental analysis of the cyclone samples were performed using the SEM and an energy dispersive analyzer for x-ray fluorescence analysis.

Results

The four particle-size distribution obtained at the flooded-bed scrubber are shown in Figure 1. The microscopically determined size distribution shows that 50% of the mass emissions are smaller than 1.6 μm in diameter. Variations in mass loading in the stack resulted in the difference between the three distributions obtained with the Andersen Stack Sampler.

Figure 2 is a transmission electron micrograph of particles from the filter sample. The large cubic particle measures 0.38 μm on a side, and the numerous small particles of γ-calcium sulfate and gypsum are less than 0.1 μm in diameter. The complete results of the selected area electron diffraction analysis are given in Table 2.

TABLE 2

Approximate Composition of Particles Collected from a Flooded-Bed Scrubber Outlet

Chemical species	Concentration
$CaSO_4 \cdot 2H_2O$	~ 70%
$CaSO_4$	~ 20%
$CaCO_3$	< 5%
Fe_3O_4 and Fe_2O_3	< 5%
SiO_2 (glass spheres)	< 5%
CaO	< 5%

The analysis of the cyclone sample collected from the Zurn scrubber showed that 83% of the mass of particulate emitted from that scrubber are smaller than 0.74 μm in diameter. X-ray fluorescence analysis on these samples indicated that the major elements are calcium and sulfur with only minor amounts of silicon and iron, which is similar to the particle composition of the flooded-bed scrubber.

Conclusions

Because short sampling times are necessary to avoid particle re-entrainment, the Andersen Stack Sampler is not useful for determining particle size-distribution from wet scrubbers.

The high concentration of small hydrated calcium sulfate crystals indicates that much of the particulate emissions from limestone wet scrubbers are being produced by evaporation of droplets containing dissolved calcium and sulfate ions. However, scrubber efficiency for solids seems very good since very little flyash was found in our samples.

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[2] Federal Register, Standards of Performance for New Stationary Sources, EPA, Volume 36, Number 159, Part 11, 17 August 1971.

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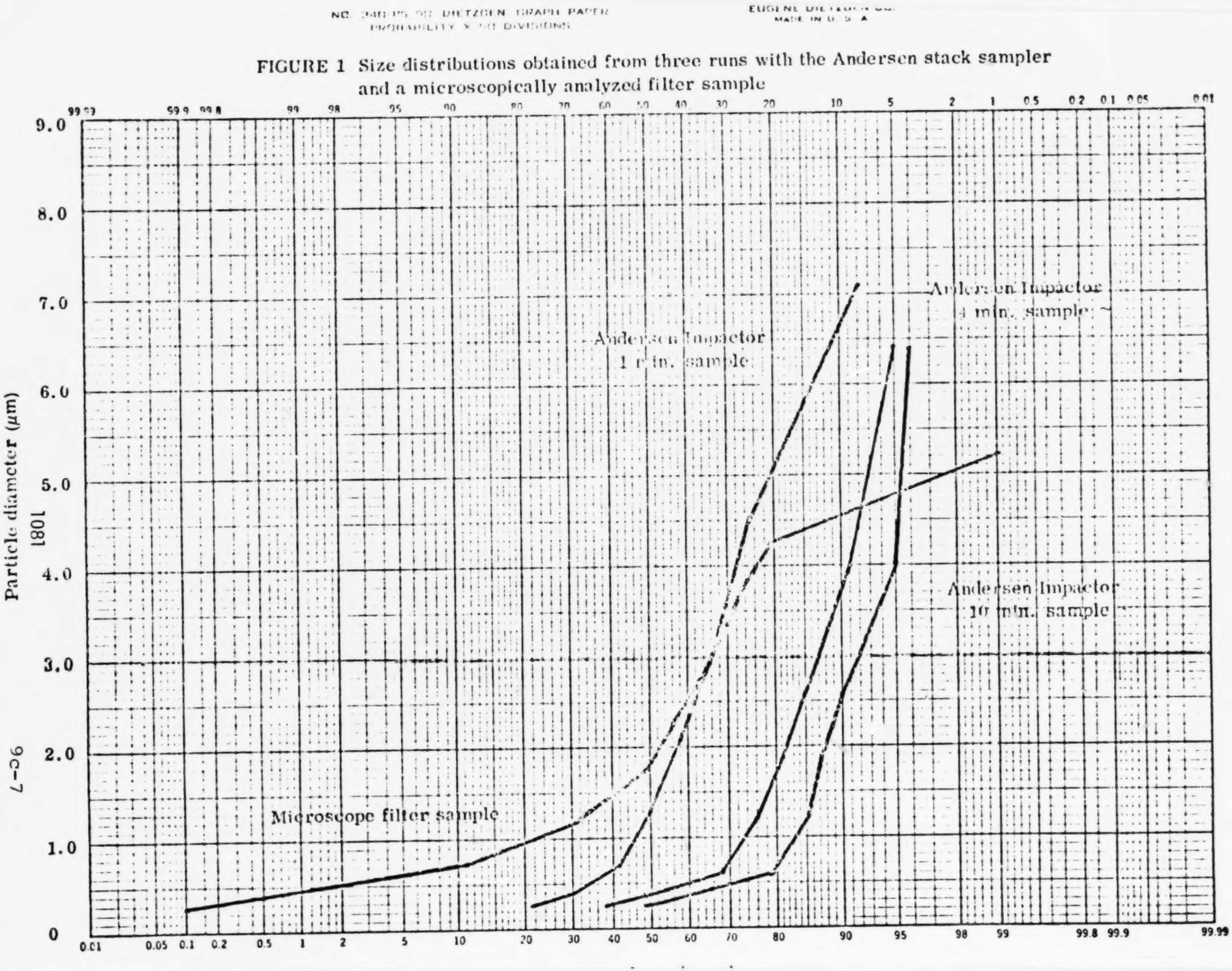
FIGURE 1 Size distributions obtained from three runs with the Andersen stack sampler and a microscopically analyzed filter sample



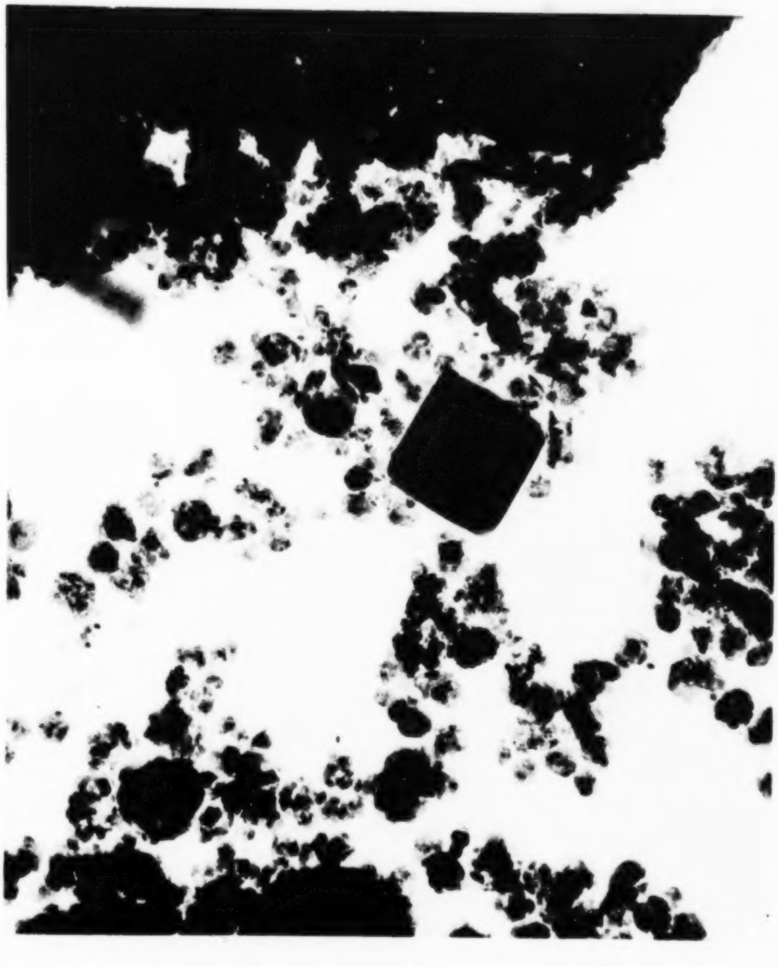


FIGURE 2 Transmission electron micrograph of particles emitted from the wet scrubber, (50,000X).

DESIGN CRITERIA FOR A SIZE-SELECTIVE SAMPLER FOR LIMESTONE WET SCRUBBERS

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SUMMARY

The reasons for and difficulties in developing a gravimetric size-selective sampler for use with a limestone wet scrubber are outlined. The expected gas stream conditions at the sampling site are described.

A parallel cyclone sampler which meets the design requirements is discussed. Methods of obtaining representative samples of particulates from the gas stream, of accurately sizing the samples, and of determining the maximum number of size cuts which can be obtained have been developed for this sampler and are described. Also included is a discussion of how data from the sampler can be used to determine the particle-size collection efficiency curves for a scrubber.

INTRODUCTION

Particle-size information is useful in the design of all particulate collection devices. The effects of size distribution of limestone moeties on gas-solid reaction kinetics makes particle-size data vital to the development of the limestone wet scrubber. As reported in a previous paper, the only commercially available size-selective sampler for use at stack conditions, the

Andersen stack sampler, does not perform satisfactorily.[1] As a result, the development of a parallel cyclone sampler for use at the EPA Alkali Scrubbing Test Facility at Shawnee was begun.[2]

Conceptual Design of a Size-Selective Sampler

A sampler should, of course, provide accurate results and avoid the particle reentrainment problem encountered with the Anderson stack sampler. It should also measure those segments of the particle-size distribution which will provide information about the fractional removal efficiency of the wet scrubber and the specific surface of the particulate. The sensitivity and resolution of the sampler should be adequate to detect significant changes in the particle-size distribution.

A small cyclone followed by a filter meets these requirements, and, by using several of these in parallel, a gravimetric size-selective sampler is obtained. The filter provides a stable low terr weight collection media upon which the particulate matter which passes the cyclone can be accurately weighed. The cyclone thereby acts as a particle-size selector for the filter.

Since a single sampling probe must transport an unbiased sample of particulate from the stack to the cyclone for fractionation, the first task in designing the sampler is determination of the conditions that produce a minimum of sample bias by particulate deposition in the transpost tube. Laboratory experiments later confirmed during a field test, proved that dust deposition can be reduced to 2% by mass with proper selection of transport tube diameter and a transport nozzle having a radius of curvature of 4 diameters. Transpost tube diameter should be selected to obtain a Reynold's number of approximately

15,000 for the tube.

The next task in the design of the cyclone sampler is the determination of the number of stages that can be used and the selection of the particle-size cut-off point (d_{50}) for each stage. Each stage of the sampler views one portion of the particle-size spectrum: the number of stages that can be used, then, is limited by the line width, or resolution of each stage, the line width being the uncertainty in knowing the collection efficiency of the device. At best, the cut points for the stages can be one line width apart over the entire size range. A more reasonable spacing would be three line widths.

Two factors affect the resolution of the collector: the error in controlling the collection parameters and the error in the calibration method. It is possible to estimate these errors from theoretical considerations and thereby determine the approximate resolution of a cyclone. By using the method of sensitivity analysis[3] to analyze the mathematical prediction equation of the cyclone collection efficiency, we found that reasonable errors in controlling the collection parameters (flow rate, viscosity, temperature, etc.) lead to variations in the cut point of 2-10%. If a scanning electron microscope is used for calibration, the calibration error can easily be kept below 0.1 μm. The sum of the calibration error and the variance in the collection parameters reduce the size resolution of a cyclone having a cut point of 1 μm to a resolution of 0.1-0.14 μm. For larger cut points, the size resolution is limited by the variance of the collection parameters; for a cut point of 4.5 μm the size resolution is about 0.14-0.49 μm. By applying these limitations to the size distribution obtained at the outlet of the Kansas Power and Light Scrubber,[1] some logical choice of the number of stages can be made. Table 1 shows that six cut points can be placed, three resolution elements apart, along the mass distribution.

TABLE 1

Cut Points and Size Resolution of Cyclone Stages

Stage	Cut point d_{50} (μm)	3 Resolution elements (μm)	% of particulate mass below d_{50}	% of particulate area below d_{50}
1	4.48	1.47	90	98
2	3.16	0.96	75	90
3	2.10	0.70	60	86
4	1.35	0.5	39	65
5	0.80	0.39	15	35
6	0.52	0.3	3	10

The outlet of the precollector functions as a gas manifold to divide the gas into seven branches. Since the gas flow in the precollector outlet is a vortex, the best aerodynamic method of dividing the flow is the use of 7 tangential outlets. An inverted cone in the middle of the outlet manifold is used to maintain the vortex motion all the way to the top of the manifold. By incorporating the filter holders into the cover plates of the small cyclones, particle losses due to deposition in the connecting tubing are minimized.

When the sampler is used at the scrubber inlet where large particles are present, a precollector to scalp large particles is used in front of the parallel stages. It is necessary to prevent large particles from entering the small cyclone where gas velocities are high and particle bounce can lead to the escape of large particles. The cut point for the precollector then should be small enough to remove most of the large particles but not so small that there is substantial overlap between the collection efficiency curve of the first stage and that of the precollector. We found that a cut point for the precollector of 6.75 μm meets the requirements.

By addition of a filter as one of the parallel stages, the mass concentration of the particulate can be determined and the total flow rate of the sampler can be easily varied to maintain isokinetic conditions.

Methods of Designing Cyclones

So that the parallel cyclones can be systematically designed, an adequate understanding of cyclone performance is necessary. A design technique which optimizes and adjusts all cyclone parameters has been developed based on the work of several German researchers.[4,5,6] This design method not only predicts the performance of the cyclone but also adjusts the cyclone geometry so that a minimum amount of energy in the form of a pressure loss is used to collect particles of a given size. The result of the optimization process is reduced turbulence in the cyclone, which should lead to sharp collection efficiency characteristics.

With a computer to aid in the calculations, three types of cyclones have been designed for the sampler. One type of cyclone serves for stages 1, 2, and 3 while another is used for stages 4, 5, and 6. The third type is used as the precollector. We estimated that the flow rate through stage 6 would have to be greater than 0.75 cfm to obtain an accurately weighable sample of particulate in 30 minutes at the lowest mass concentration expected. Table 2 shows the operating conditions for each stage and the precollector.

TABLE 2

Operating Conditions for Each Cyclone

Stage	Flow rate (cfm)	Pressure drop (in. of H_2O)
1	0.475	0.114
2	0.675	0.248
3	1.00	0.605
4	0.400	2.63
5	0.650	7.79
6	0.875	15.31
precollector	5.025	0.165

Maintaining a constant cut point for each cyclone is a complex task since the cut point depends on the gas velocity, density, viscosity, and wall friction in the cyclone. In practice it has been found that as particulate deposits on the walls of the cyclone, the pressure loss in the cyclone drops, indicating a reduction in gas velocity. This leads to the idea that perhaps the best way of maintaining a constant cut point would be maintaining a constant pressure loss in the cyclone. Therefore the pressure drop across each stage is monitored by magnihelic differential pressure gages.

A conceptual design for the entire sampling train shows in Figures 1 and 2. The sampling train consists of three units: the sample box which contains the cyclone, a control unit which contains pumps, and gas metering equipment and a cooling supply system for the water vapor traps.

Results of Preliminary Testing

A cyclone having near optimum geometry was designed and constructed. A field test on a pilot-plant wet scrubber, discussed in a previous paper, was carried out to determine the performance of the cyclone. We had calculated that for a flow rate of 0.8 cfm the small cyclone would have a pressure drop of 27 in. water; however, we found its actual drop to be 17 in. water, indicating that the frictional losses in the cyclone walls had been underestimated. The design equations also predicted that 50% collection efficiency would occur at 0.44-μm particle diameter for a 1-cfm flow rate. As is seen in Figure 3, the actual 50% collection efficiency occurred for 0.74 μm. This is, again, due to the increased wall losses causing reduced velocities and collection efficiency in the cyclone.

A measure of the steepness of the collection efficiency curve for a device is given by the geometric standard derivation of the collection efficeincy S where

$$S = \frac{\text{Particle diameter at 50\% efficiency}}{\text{Particle diameter at 84.13\% efficiency}}$$

We are gratified to note that the optimization procedure for the cyclone design produced a very steep efficiency curve having a geometric standard deviation of 0.94. This surpasses the performance reported for several cyclones[7,8,9] as well as for inertial impactors.[10]

Conclusions

Undoubtedly a parallel cyclone sampler can be built using the design techniques developed thus far. The inability to accurately predict performance merely means that emperical calibrations methods will have to be used. Before better predictions can be made, however, a better understanding of friction losses in cyclones will have to be obtained.

Footnotes

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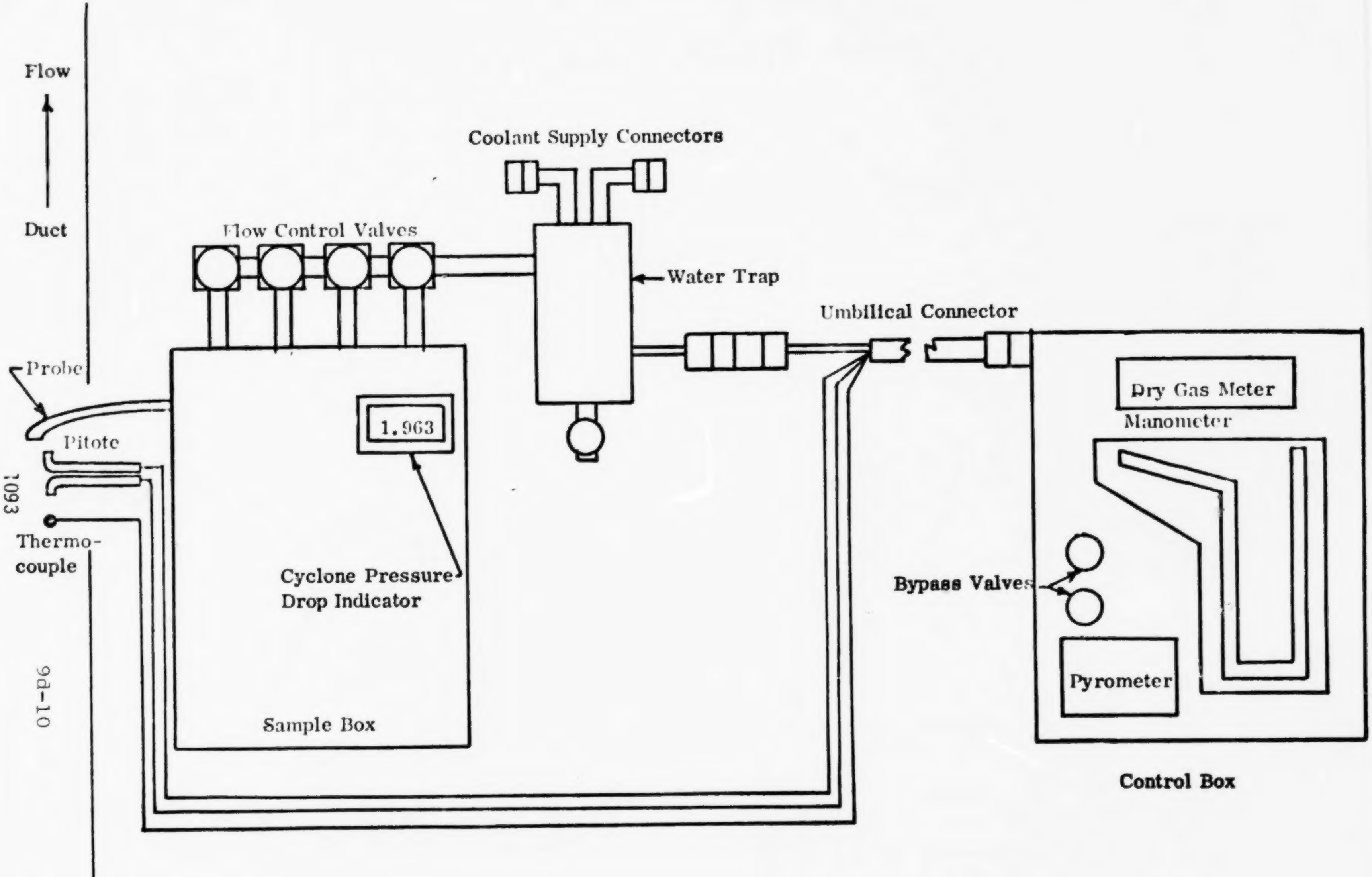


FIGURE 1 Layout of size selective gravimetric sampler

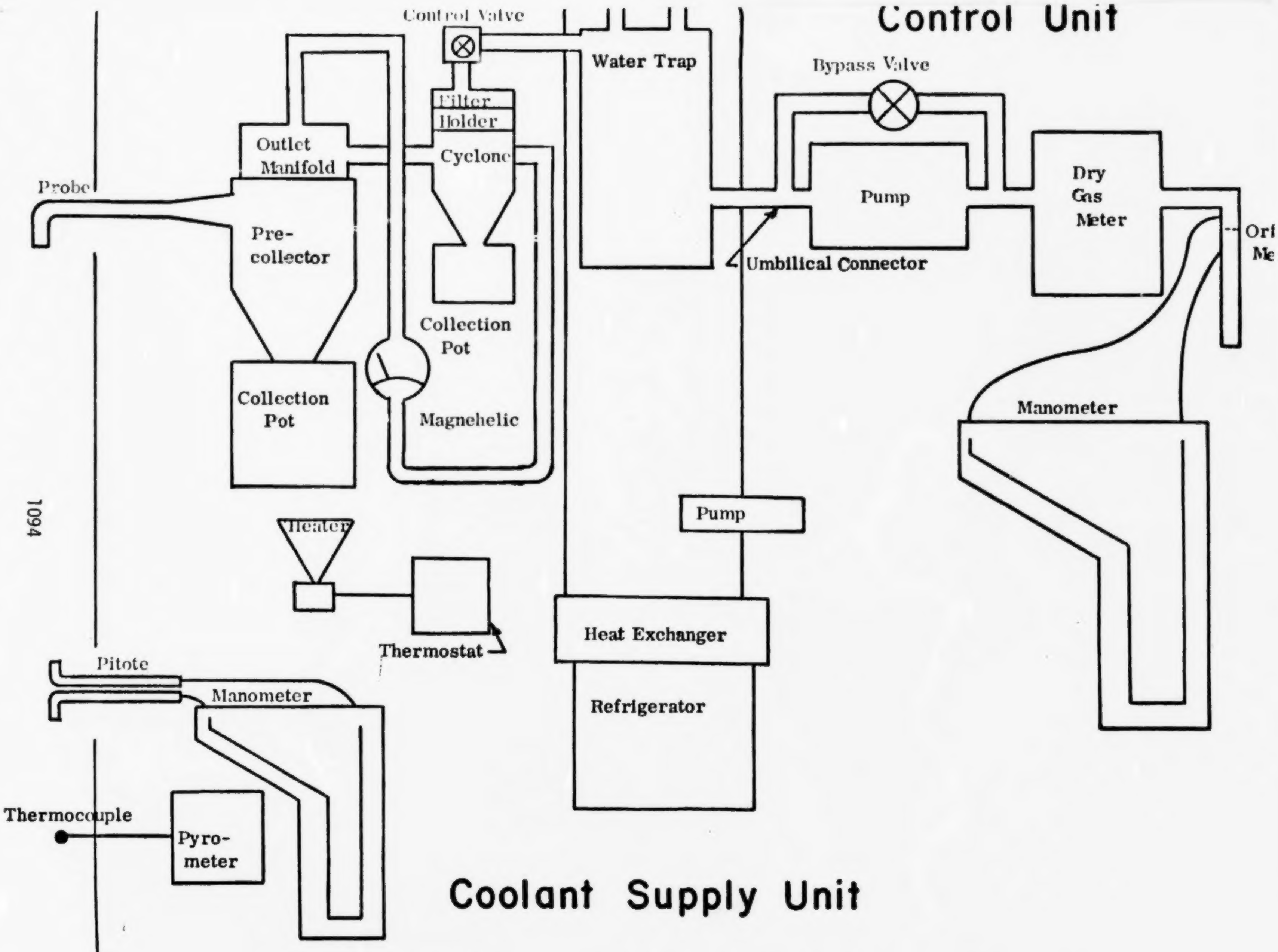
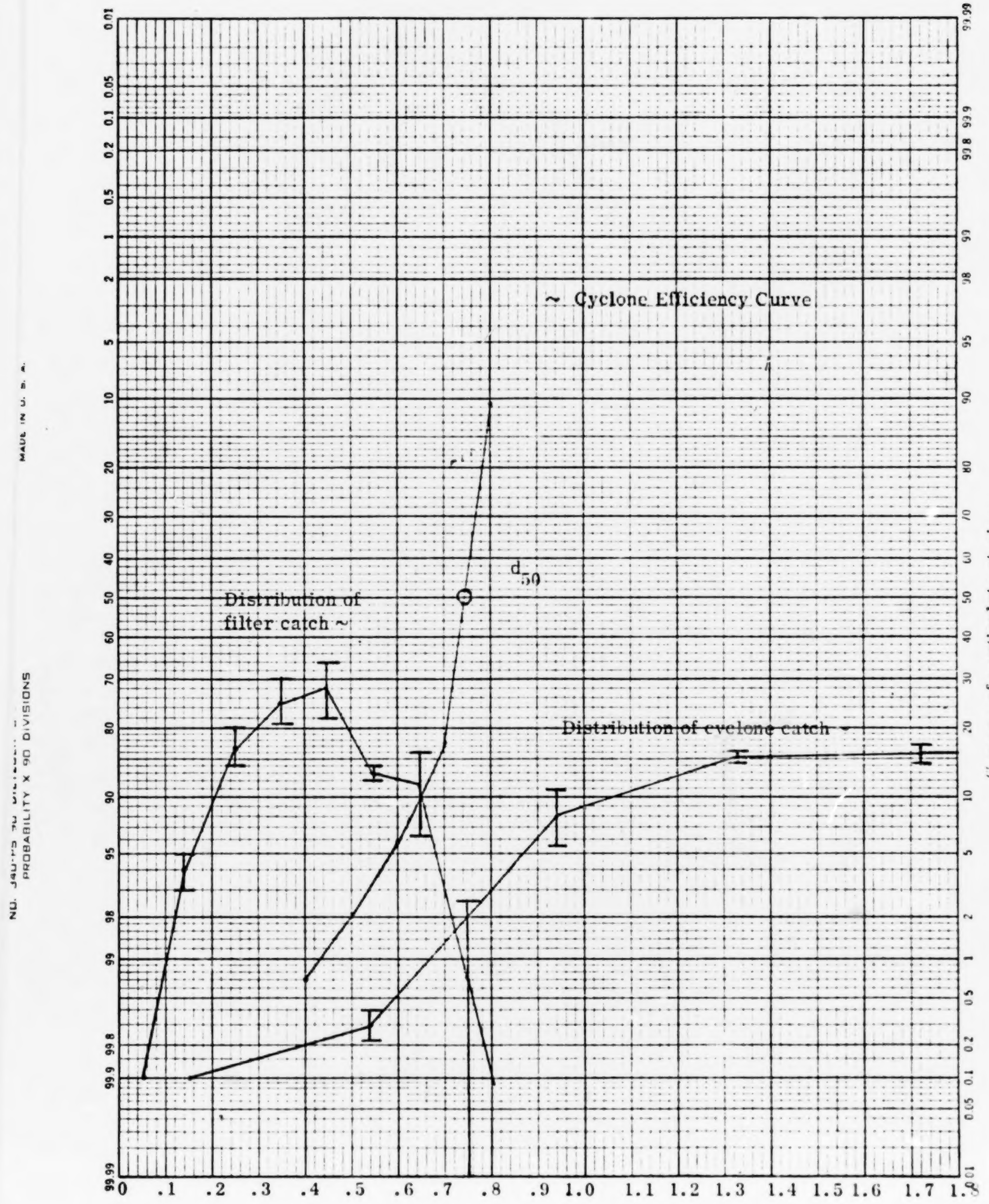


FIGURE 2 Components of size selective sample

FIGURE 3 Size distribution of TVA samples collected with small cyclone



INSTRUMENTAL METHODS FOR FLUE GAS ANALYSIS

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The application of continuous monitoring instrumentation to pilot plant and fuel scale evaluations of control technologies require careful consideration of the effects of the source and sampling system on overall accuracy of the measurement. In general, to monitor the mass flow rate of pollutants in flue gas, the following three problem areas must be considered.

1. Sample Acquisition
2. Sample Handling
3. Instrument Selection

1. Sample Acquisition:

The major problem in the precision determination of pollutant mass flow rate (lbs/hr) is the variation of the species concentration which may exist spacially in a large duct as a result of air infiltration and poor mixing (stratification). In the course of OAP's extensive studies of coal fired power plant effluents, a large number of carbon dioxide concentration profiles within large ducts were obtained at various sampling locations.

Typical sampling locations are illustrated in Figure 1 for a power plant. The two most common sampling locations are at the inlet and at the outlet of control equipment. Infiltration of air generally occurs within and post the air pre-heater. In Figure 2 and Table I, examples of homogeneous and stratified carbon dioxide profiles are shown. As can be seen in Figure 3, the probability of determining the concentration of a species within 15% with a single probe is fifty percent. With nine probes, one achieves a 99+% probability of determining the pollutant concentration within 15%.

Stratified flow in pilot plant operations can be avoided by installation of gas mixing equipment such as venturi, perforated plate, vanes, etc. at a cost of about $500-$1500 @ 3000 acfm. This expedient will assure the most accurate measurement possible of the concentration of the pollutant with a single point sample probe. To determine the total gas flow, a gas metering venturi is acceptable.

At a full scale power plant, it is unrealistic to modify the plant; therefore, the mass flow rate can best be determined by careful selection of the sampling site and verification of sampling conditions by complete characterization of the velocity profile and determination of whether stratification exists.

The best sites for pollutant concentration and determination of the velocity profile are not necessarily identical; one approach which can be used is:

a. Determination of SO_2 or NOx concentration along with the CO_2 concentration post the economizer but prior to the air preheater.

b. Determination of the velocity profile at a location move amenable to a velocity traverse. This will yield the total gas volumetric flow at the location.

c. The volumetric flow of gas at the economizer is given by volumetric flow at economizer = volumetric flow (from velocity data) x $\frac{CO_2 \text{ (at traverse)}}{CO_2 \text{ (at economizer)}}$

2. Sample Handling

Having selected and evaluated a site, the next consideration is extraction of samples.

Probes:

The sampling probe design is dictated by temperature. It can be as simple as a 1/2-inch O.D. stainless steel tube for temperature 350°F and above, or as complex as a shielded in the stack filter-probe combination for temperatures below 350°F to minimize reactive losses of SO_2

Filters:

All instruments which utilize optical principles to determine the pollutant concentration require the removal of particulate matter. Particulate matter is removed by passing the particulate laden-gas stream through a positive filter. A silicon carbide filter which has a 90% collection efficiency at 5μ have been found to be practical. These filters can be mounted internal or external of the ducting; since the average working life of the filters is 3-4 weeks (at 5-7 grains/scf and 2 cfh flow), the external stack filter is recommended for ease of replacement of the filter and minimum down time. The filter assembly should be maintained at 300-350°F to eliminate reactive SO_2 losses with the filtering media.

A potential problem particular to wet scrubbers might be observed post the device. If there is substantial liquid re-entrainment and poor mist eliminator efficiency, the saturated scrubber liquor droplets will enter the probe and be collected on the filtering media. At 300-350°F, evaporation of the water will leave a residual deposit of $CaSO_4$, $CaSO_42H_2O$, and $CaCO_3$ platlets which will plug the filter. Filter pluggage was observed during manual particulate sampling at Kansas Power and Light. It will also occur using the filters described above; to reduce the probability of this type of pluggage, high turbulence in the probe to promote droplet evaporation is recommended.

Sampling Lines and Water Vapor Condensors

The sampling lines can be constructed of heat traced teflon or stainless steel. The sampling lines should be maintained above the dew point of the flue gas, 300-350°F. Stress corrosion has been observed in the sampling lines (304 stainless steel) used at the TVA dry limestone injection tests. The need for frequent replacement of the stainless steel tubing makes the heat traced teflon, although initially more expensive, the most desirable material of construction. The use of rubber on PVC tubing is not recommended since absorption of SO_2 on tube walls occurs in these materials.

For those who select non-dispersive infrared (NDIR) as the pollutant monitor, a condensing system is required to remove water vapor which is a positive interference. A sample NDIR has a rejection ratio of 100; that is, 100 ppm of water vapor yields a signal equivalent to 1 ppm of SO_2. A condensor held at $0^\circ \pm 1^\circ C$ will contribute a ± 4 ppm signal of SO_2 equivalent water vapor. At 1000 ppm SO_2 or greater, typical of the scrubber inlet this error is insignificant, but with 90% control of a 1000 ppm inlet SO_2 concentration, it will yield a ± 4% error in the SO_2 level at the outlet.

Gas Pumps

Either bellows type or other leakless air moving pump is acceptable. The pump is located prior to the detection system.

Response Time

All of the components of a sampling system have been covered, these elements should be so constructed such that the desired system response time is achieved. The system response time is defined as:

> The time interval from a step change in pollutant concentration at the probe inlet to a recording of 90% of the ultimate recorded output.

By suitably adjusting the volume of the sample handling system and/or the volumetric flow through the sampling system a wide range of system response times are achievable. For a typical NDIR sampling analysis system, the sample handling system has a total volume of 0.5 cu ft (assuming 100' 1/2-inch I.D. tubing, filter, and 0.3 cu ft cooler volume). The response time of the system, assuming plug flow and 2 cfh pumping capacity, normally supplied with instrument, is 15 minutes.

In Figure 4, a high volume pump about 20 cfh is used to extract the sample and draw it through the filter and cooler. The water and particulate free stream is then sampled by the 2 cfh pump. This will reduce the system response time to 1.5 minutes with a sample system of 0.5 cu ft.

3. Instrumentation

The Office of Air Programs had funded field evaluation of commercially available sulfur dioxide and nitrogen oxide monitors. These studies were conducted at coal fired power plants; the sulfur oxide study at a steam station burning 0.5% sulfur coal; the nitrogen oxides study at a coal fired station with approximately 200 ppm NOx emissions. Preliminary results of these studies are shown in Table II.

The table also shows that for sulfur dioxide NDIR's or DNUV's are of comparable accuracy and reliability. For NO, NDIR; for NO_2 NDUV; presently only NDUV for total NOx; however, this is batch operation and the 10 minute reactor time must be added to system response time. In addition to the instrumentation described above, flue gas analysis could be performed by gas chromatography, mass spectroscopy, dispersive infrared, etc. None of these are presently available as commercially tested units.

Instrument types, found to be effective for data collection for engineering analysis for control systems development of SO_2 and NOx flue gas control equipment, include:

SO_2--NDIR and NDUV,
NO --NDIR and NDUV, and
NOx--NDUV.

The NDUV is sensitive to NO_2 and the commercially available instrument provides integral catalytic oxidation of NO to NO_2.

Overall Conclusions

The overall conclusions which can be reached are:

1. Extreme care must be exercised in the choice of sampling location and each location should be completely characterized.
2. The probe, filter, and sampling lines must be held above the dew point of the gas stream.
3. Using vendor supplied sample conditioning equipment and gas pumps, system response times are greater than 10 minutes.
4. For sulfur dioxide monitoring, NDIR's or NDUV's are effective.
5. For nitrogen oxides, NDUV is effective if 10 minute cycle times are acceptable; for continuous analysis NDIR's are effective (note: total nitrogen oxides will be NO; NDIR's are insensitive to NO2).

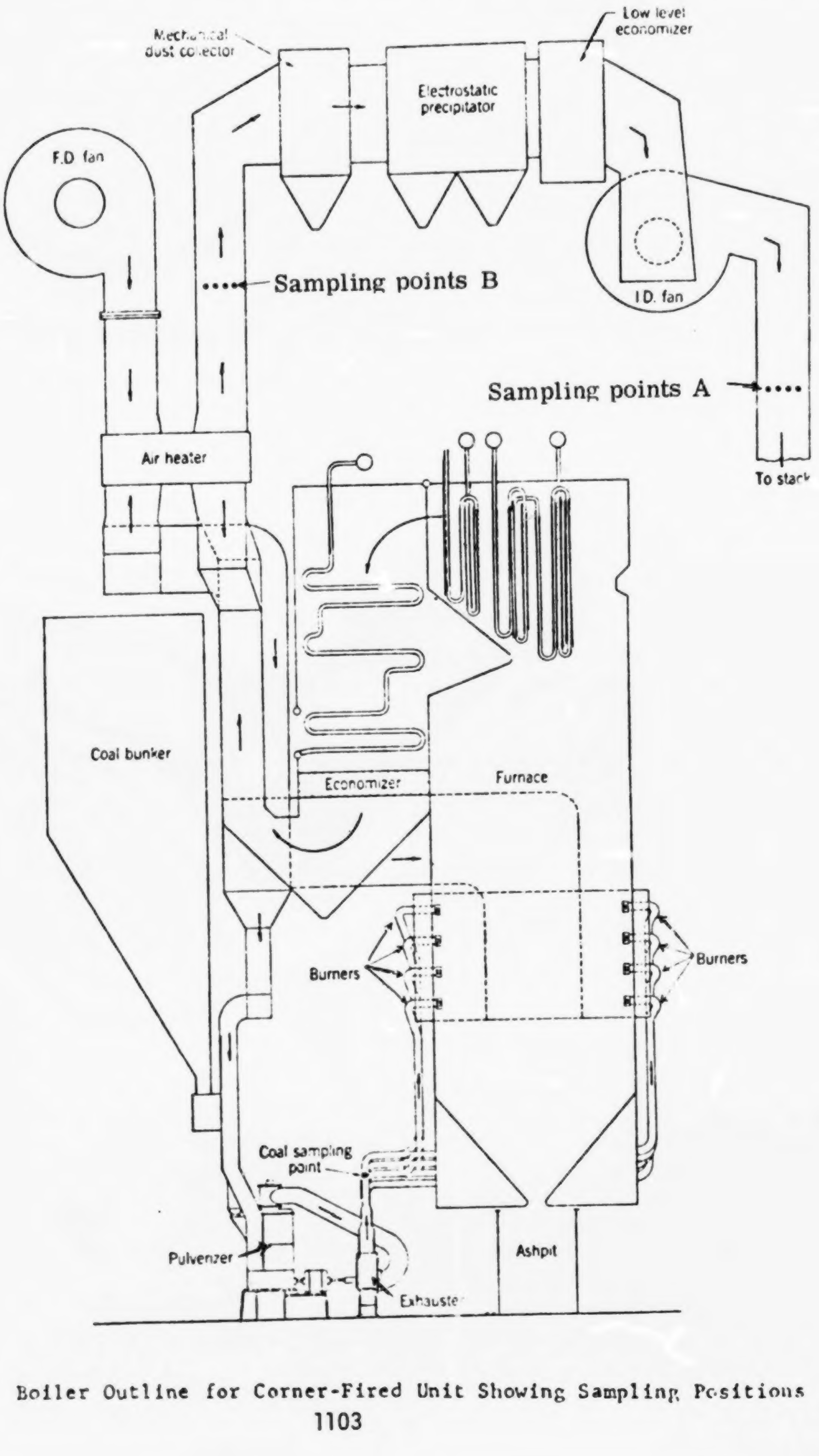
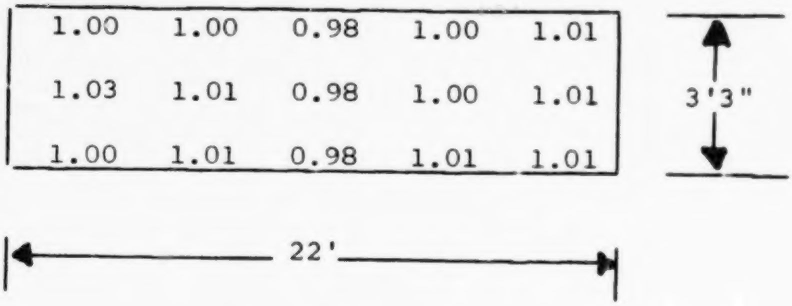


Figure 1 Boiler Outline for Corner-Fired Unit Showing Sampling Positions

HOMOGENEOUS

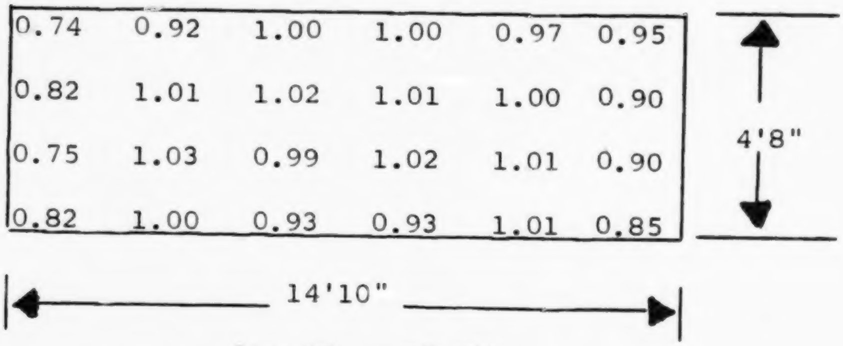


1.00	1.00	0.98	1.00	1.01
1.03	1.01	0.98	1.00	1.01
1.00	1.01	0.98	1.01	1.01

Avg CO_2 = 11.7%

CV = 1.9%

STRATIFIED



0.74	0.92	1.00	1.00	0.97	0.95
0.82	1.01	1.02	1.01	1.00	0.90
0.75	1.03	0.99	1.02	1.01	0.90
0.82	1.00	0.93	0.93	1.01	0.85

Avg CO_2 = 12.6%

CV = 9.3%

Random selection from six plants.

Figure 2. Normalized CO_2 Traverse Data at Dust Collector of Coal-Fired Power Plants.

TABLE I. OBSERVED COEFFICIENT OF VARIATION FOR CO_2 TRAVERSE FOR VARIOUS COAL-FIRED PLANTS

Plant No.	Type of Boiler Firing	Dust Collection Equipment	Sampling Location	No. of Traverse Points	CO_2 (CV) %
1	Horizontally opposed	C	I	24	9.3
			O	12	2.3, 1.4
2	Cyclone	E	I	24	4.6
			O	24	3.2
3	Spreader stoker	C	I	18	1.5
			O	9	1.02
4	Corner	C, E	I	18	8.8
			O	12	0.97
5	Vertical	C, E	I	24	7.1
			O	12	3.2

C=Cyclone
E=Electrostatic precipitator
I=Dust collector inlet
O=Dust collector outlet

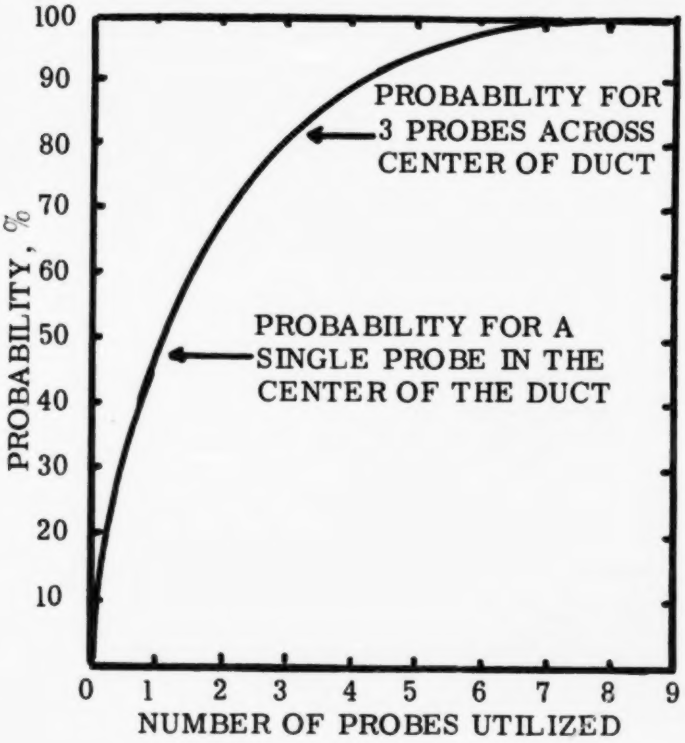


Figure 3. Probability of Obtaining an Accuracy Within 15% of 9-Point Analysis for O_2 in a Large Duct

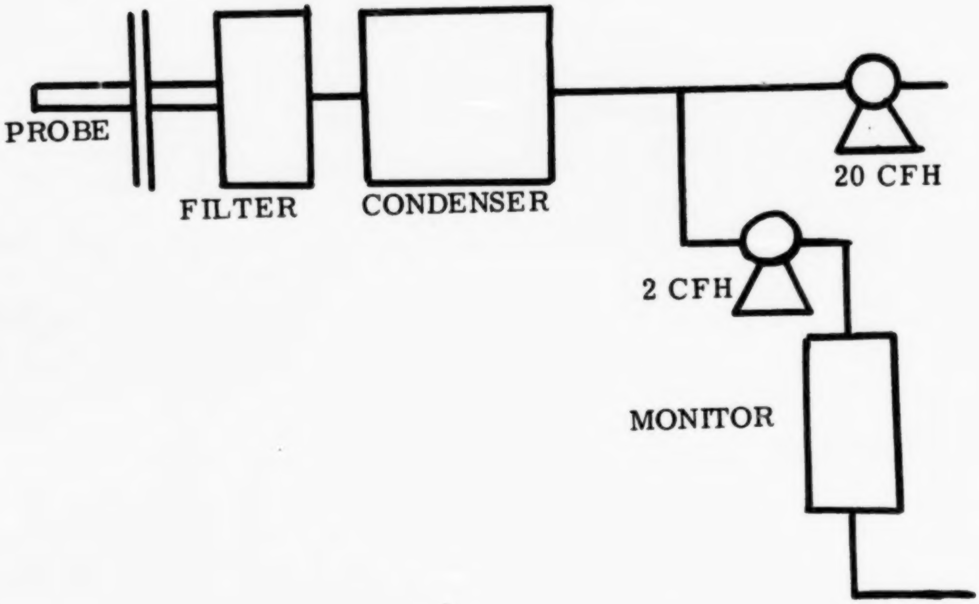


Figure 4. Fast-Response Sampling System.

TABLE II. SULFUR DIOXIDE MONITORS

Detection Principle	Instrument Response Time (1)	Reliability (2) MTF	Accuracy
NDIR	Good	351 hrs.	Good
NDUV	Good	322 hrs.	Good
Conductrometric	Poor	67.1 hrs.	Good
Coulometric	Good	569 hrs.	Good
Electrochemical	Good	Poor	Good

Nitrogen Oxide Monitor

Detection Principle	Response Time	Reliability, MTF. (2)	Accuracy
NDIR	Good	Very Good (3)	Good
NDUV	Good	Very Good (3)	Good
Electrochemical	Good	Poor	Good

(1) Time interval from a step change in the pollutant in concentration at the instrument inlet to a recording of 90% of the ultimate recorded output (∿3 sec.).

(2) Mean time between failure

(3) No failures during test

EPA RECOMMENDED SOURCE TEST METHODS FOR NEW SOURCE PERFORMANCE STANDARDS TESTING

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Applied Technology Division
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Prepared for
Second International Lime/Limestone
Wet Scrubbing Symposium
New Orleans, Louisiana
November 8-12, 1971

EPA RECOMMENDED SOURCE TEST METHODS FOR NEW SOURCE PERFORMANCE STANDARDS TESTING

The text of this paper consisted of an explanation of the Standards of Performance for New Stationary Sources proposed by the Environmental Protection Agency and established by the Clean Air Act as Ammended. Gene Smith used the Federal Register, Vol. 36, No. 247--Thursday, December 23, Part II as his reference material, which he handed out during the symposium.

federal register

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PART II

THE NATIONAL ARCHIVES OF THE UNITED STATES
1934

ENVIRONMENTAL PROTECTION AGENCY

■

Standards of Performance for New Stationary Sources

Title 40—PROTECTION OF ENVIRONMENT

Chapter I—Environmental Protection Agency

SUBCHAPTER C—AIR PROGRAMS

PART 60—STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

On August 17, 1971 (36 F.R. 15704) pursuant to section 111 of the Clean Air Act as amended, the Administrator proposed standards of performance for steam generators, portland cement plants, incinerators, nitric acid plants, and sulfuric acid plants. The proposed standards, applicable to sources the construction or modification of which was initiated after August 17, 1971, included emission limits for one or more of four pollutants (particulate matter, sulfur dioxide, nitrogen oxides, and sulfuric acid mist) for each source category. The proposal included requirements for performance testing, stack gas monitoring, record keeping and reporting, and procedures by which EPA will provide preconstruction review and determine the applicability of the standards to specific sources.

Interested parties were afforded an opportunity to participate in the rule making by submitting comments. A total of more than 200 interested parties, including Federal, State, and local agencies, citizens groups, and commercial and industrial organizations submitted comments. Following a review of the proposed regulations and consideration of the comments, the regulations, including the appendix, have been revised and are being promulgated today. The principal revisions are described below:

1. Particulate matter performance testing procedures have been revised to eliminate the requirement for impingers in the sampling train. Compliance will be based only on material collected in the dry filter and the probe preceding the filter. Emission limits have been adjusted as appropriate to reflect the change in test methods. The adjusted standards require the same degree of particulate control as the originally proposed standards.

2. Provisions have been added whereby alternative test methods can be used to determine compliance. Any person who proposes the use of an alternative method will be obliged to provide evidence that the alternative method is equivalent to the reference method.

3. The definition of modification, as it pertains to increases in production rate and changes of fuels, has been clarified. Increases in production rates up to design capacity will not be considered a modification nor will fuel switches if the equipment was originally designed to accommodate such fuels. These provisions will eliminate inequities where equipment had been put into partial operation prior to the proposal of the standards.

4. The definition of a new source was clarified to include construction which is completed within an organization as well as the more common situations where the facility is designed and constructed by a contractor.

5. The provisions regarding requests for EPA plan review and determination of construction or modification have been modified to emphasize that the submittal of such requests and attendant information is purely voluntary. Submittal of such a request will not bind the operator to supply further information; however, lack of sufficient information may prevent the Administrator from rendering an opinion. Further provisions have been added to the effect that information submitted voluntarily for such plan review or determination of applicability will be considered confidential, if the owner or operator requests such confidentiality.

6. Requirements for notifying the Administrator prior to commencing construction have been deleted. As proposed, the provision would have required notification prior to the signing of a contract for construction of a new source. Owners and operators still will be required to notify the Administrator 30 days prior to initial operation and to confirm the action within 15 days after startup.

7. Revisions were incoporated to permit compliance testing to be deferred up to 60 days after achieving the maximum production rate but no longer than 180 days after initial startup. The proposed regulation could have required testing within 60 days after startup but defined startup as the beginning of routine operation. Owners or operators will be required to notify the Administrator at least 10 days prior to compliance testing so that an EPA observer can be on hand. Procedures have been modified so that the equipment will have to be operated at maximum expected production rate, rather than rated capacity, during compliance tests.

8. The criteria for evaluating performance testing results have been simplified to eliminate the requirement that all values be within 35 percent of the average. Compliance will be based on the average of three repetitions conducted in the specified manner.

9. Provisions were added to require owners or operators of affected facilities to maintain records of compliance tests, monitoring equipment, pertinent analyses, feed rates, production rates, etc. for 2 years and to make such information available on request to the Administrator. Owners or operators will be required to summarize the recorded data daily and to convert recorded data into the applicable units of the standard.

10. Modifications were made to the visible emission standards for steam generators, cement plants, nitric acid plants, and sulfuric acid plants. The Ringelmann standards have been deleted; all limits will be based on opacity. In every case, the equivalent opacity will be at least as stringent as the proposed Ringelmann number. In addition, requirements have been altered for three of the source categories so that allowable emissions will be less than 10 percent opacity rather than 5 percent or less opacity. There were many comments that observers could not accurately evaluate emissions of 5 percent opacity. In addition, drafting errors in the proposed visible emission limits for cement kilns and steam generators were corrected. Steam generators will be limited to visible emissions not greater than 20 percent opacity and cement kilns to not greater than 10 percent opacity.

11. Specifications for monitoring devices were clarified, and directives for calibration were included. The instruments are to be calibrated at least once a day, or more often if specified by the manufacturer. Additional guidance on the selection and use of such instruments will be provided at a later date.

12. The requirement for sulfur dioxide monitoring at steam generators was deleted for those sources which will achieve the standard by burning low-sulfur fuel, provided that fuel analysis is conducted and recorded daily. American Society for Testing and Materials sampling techniques are specified for coal and fuel oil.

13. Provisions were added to the steam generator standards to cover those instances where mixed fuels are burned. Allowable emissions will be determined by prorating the heat input of each fuel, however, in the case of sulfur dioxide, the provisions allow operators the option of burning low-sulfur fuels (probably natural gas) as a means of compliance.

14. Steam generators fired with lignite have been exempted from the nitrogen oxides limit. The revision was made in view of the lack of information on some types of lignite burning. When more information is developed, nitrogen oxides standards may be extended to lignite fired steam generators.

15. A provision was added to make it explicit that the sulfuric acid plant standards will not apply to scavenger acid plants. As stated in the background document, APTD 0711, which was issued at the time the proposed standards were published, the standards were not meant to apply to such operations, e.g., where sulfuric acid plants are used primarily to control sulfur dioxide or other sulfur compounds which would otherwise be vented into the atmosphere.

16. The regulation has been revised to provide that all materials submitted pursuant to these regulations will be directed to EPA's Office of General Enforcement.

17. Several other technical changes have also been made. States and interested parties are urged to make a careful reading of these regulations.

As required by section 111 of the Act, the standards of performance promulgated herein "reflect the degree of emission reduction which (taking into account the cost of achieving such reduction) the Administrator determines has been adequately demonstrated". The standards of performance are based on stationary source testing conducted by the Environmental Protection Agency and/or contractors and on data derived from various other sources, including the available technical literature. In the comments on the proposed standards, many questions were raised as to costs and demonstrated capability of control systems to meet the standards. These comments have been evaluated and investigated, and it is the Administrator's judgment that emission control systems capable of meeting the standards have been adequately demonstrated and that the standards promulgated herein are achievable at reasonable costs.

The regulations establishing standards of performance for steam generators, incinerators, cement plants, nitric acid plants, and sulfuric acid plants are hereby promulgated effective on publication and apply to sources, the construction or modification of which was commenced after August 17, 1971.

Dated: December 16, 1971.

WILLIAM D. RUCKELSHAUS,
Administrator,
Environmental Protection Agency.

A new Part 60 is added to Chapter I, Title 40, Code of Federal Regulations, as follows:

Subpart A—General Provisions

Sec.
60.1 Applicability.
60.2 Definitions.
60.3 Abbreviations.
60.4 Address.
60.5 Determination of construction or modification.
60.6 Review of plans.
60.7 Notification and recordkeeping.
60.8 Performance tests.
60.9 Availability of information.
60.10 State authority.

Subpart D—Standards of Performance for Fossil Fuel-Fired Steam Generators

60.40 Applicability and designation of affected facility.
60.41 Definitions.
60.42 Standard for particulate matter.
60.43 Standard for sulfur dioxide.
60.44 Standard for nitrogen oxides.
60.45 Emission and fuel monitoring.
60.46 Test methods and procedures.

Subpart E—Standards of Performance for Incinerators

60.50 Applicability and designation of affected facility.
60.51 Definitions.
60.52 Standard for particulate matter.
60.53 Monitoring of operations.
60.54 Test methods and procedures.

Subpart F—Standards of Performance for Portland Cement Plants

60.60 Applicability and designation of affected facility.
60.61 Definitions.
60.62 Standard for particulate matter.
60.63 Monitoring of operations.
60.64 Test methods and procedures.

Subpart G—Standards of Performance for Nitric Acid Plants

60.70 Applicability and designation of affected facility.
60.71 Definitions.
60.72 Standard for nitrogen oxides.
60.73 Emission monitoring.
60.74 Test methods and procedures.

Subpart H—Standards of Performance for Sulfuric Acid Plants

60.80 Applicability and designation of affected facility.
60.81 Definitions.
Sec.
60.82 Standard for sulfur dioxide.
60.83 Standard for acid mist.
60.84 Emission monitoring.
60.85 Test methods and procedures.

APPENDIX—TEST METHODS

Method 1—Sample and velocity traverses for stationary sources.
Method 2—Determination of stack gas velocity and volumetric flow rate (Type S pitot tube).
Method 3—Gas analysis for carbon dioxide, excess air, and dry molecular weight.
Method 4—Determination of moisture in stack gases.
Method 5—Determination of particulate emissions from stationary sources.
Method 6—Determination of sulfur dioxide emissions from stationary sources.
Method 7—Determination of nitrogen oxide emissions from stationary sources.
Method 8—Determination of sulfuric acid mist and sulfur dioxide emissions from stationary sources.
Method 9—Visual determination of the opacity of emissions from stationary sources.

AUTHORITY: The provisions of this Part 60 issued under sections 111, 114, Clean Air Act; Public Law 91-604, 84 Stat. 1713.

Subpart A—General Provisions

§ 60.1 Applicability.

The provisions of this part apply to the owner or operator of any stationary source, which contains an affected facility the construction or modification of which is commenced after the date of publication in this part of any proposed standard applicable to such facility.

§ 60.2 Definitions.

As used in this part, all terms not defined herein shall have the meaning given them in the Act:

(a) "Act" means the Clean Air Act (42 U.S.C. 1857 et seq., as amended by Public Law 91-604, 84 Stat. 1676).

(b) "Administrator" means the Administrator of the Environmental Protection Agency or his authorized representative.

(c) "Standard" means a standard of performance proposed or promulgated under this part.

(d) "Stationary source" means any building, structure, facility, or installation which emits or may emit any air pollutant.

(e) "Affected facility" means, with reference to a stationary source, any apparatus to which a standard is applicable.

(f) "Owner or operator" means any person who owns, leases, operates, controls, or supervises an affected facility or a stationary source of which an affected facility is a part.

(g) "Construction" means fabrication, erection, or installation of an affected facility.

(h) "Modification" means any physical change in, or change in the method of operation of, an affected facility which increases the amount of any air pollutant (to which a standard applies) emitted by such facility or which results in the emission of any air pollutant (to which a standard applies) not previously emitted, except that:

(1) Routine maintenance, repair, and replacement shall not be considered physical changes, and

(2) The following shall not be considered a change in the method of operation:

(i) An increase in the production rate, if such increase does not exceed the operating design capacity of the affected facility;

(ii) An increase in hours of operation;

(iii) Use of an alternative fuel or raw material if, prior to the date any standard under this part becomes applicable to such facility, as provided by § 60.1, the affected facility is designed to accommodate such alternative use.

(i) "Commenced" means that an owner or operator has undertaken a continuous program of construction or modification or that an owner or operator has entered into a binding agreement or contractual obligation to undertake and complete, within a reasonable time, a continuous program of construction or modification.

(j) "Opacity" means the degree to which emissions reduce the transmission of light and obscure the view of an object in the background.

(k) "Nitrogen oxides" means all oxides of nitrogen except nitrous oxide, as measured by test methods set forth in this part.

(l) "Standard of normal conditions" means 70° Fahrenheit (21.1° centigrade) and 29.92 in. Hg (760 mm. Hg).

(m) "Proportional sampling" means sampling at a rate that produces a constant ratio of sampling rate to stack gas flow rate.

(n) "Isokinetic sampling" means sampling in which the linear velocity of the gas entering the sampling nozzle is equal to that of the undisturbed gas stream at the sample point.

(o) "Startup" means the setting in operation of an affected facility for any purpose.

§ 60.3 Abbreviations.

The abbreviations used in this part have the following meanings in both capital and lower case:

B.t.u.—British thermal unit.
cal.—calorie(s).
c.f.m.—cubic feet per minute.
CO_2—carbon dioxide.
g.—gram(s).
gr.—grain(s).
mg.—milligram(s).
mm.—millimeter(s).
l.—liter(s).
nm.—nanometer(s), —10^{-9} meter.
μg.—microgram(s), 10^{-6} gram.
Hg.—mercury.
in.—inch(es).
K—1,000.
lb.—pound(s).
ml.—milliliter(s).
No.—number.
%—percent.
NO—nitric oxide.
NO_2—nitrogen dioxide.
NO_x—nitrogen oxides.
NM^3—normal cubic meter.
s.c.f.—standard cubic feet.
SO_2—sulfur dioxide.
H_2SO_4—sulfuric acid.
SO_3—sulfur trioxide.

ft.^{3}—cubic feet.
ft.^{2}—square feet.
min.—minute(s).
hr.—hour(s).

§ 60.4 Address.

All applications, requests, submissions, and reports under this part shall be submitted in triplicate and addressed to the Environmental Protection Agency, Office of General Enforcement, Waterside Mall SW., Washington, DC 20460.

§ 60.5 Determination of construction or modification.

When requested to do so by an owner or operator, the Administrator will make a determination of whether actions taken or intended to be taken by such owner or operator constitute construction or modification or the commencement thereof within the meaning of this part.

§ 60.6 Review of plans.

(a) When requested to do so by an owner or operator, the Administrator will review plans for construction or modification for the purpose of providing technical advice to the owner or operator.

(b) (1) A separate request shall be submitted for each affected facility.

(2) Each request shall (i) identify the location of such affected facility, and (ii) be accompanied by technical information describing the proposed nature, size, design, and method of operation of such facility, including information on any equipment to be used for measurement or control of emissions.

(c) Neither a request for plans review nor advice furnished by the Administrator in response to such request shall (1) relieve an owner or operator of legal responsibility for compliance with any provision of this part or of any applicable State or local requirement, or (2) prevent the Administrator from implementing or enforcing any provision of this part or taking any other action authorized by the Act.

§ 60.7 Notification and record keeping.

(a) Any owner or operator subject to the provisions of this part shall furnish the Administrator written notification as follows:

(1) A notification of the anticipated date of initial startup of an affected facility not more than 60 days or less than 30 days prior to such date.

(2) A notification of the actual date of initial startup of an affected facility within 15 days after such date.

(b) Any owner or operator subject to the provisions of this part shall maintain for a period of 2 years a record of the occurrence and duration of any startup, shutdown, or malfunction in operation of any affected facility.

§ 60.8 Performance tests.

(a) Within 60 days after achieving the maximum production rate at which the affected facility will be operated, but not later than 180 days after initial startup of such facility and at such other times as may be required by the Administrator under section 114 of the Act, the owner or operator of such facility shall conduct performance test(s) and furnish the Administrator a written report of the results of such performance test(s).

(b) Performance tests shall be conducted and results reported in accordance with the test method set forth in this part or equivalent methods approved by the Administrator; or where the Administrator determines that emissions from the affected facility are not susceptible of being measured by such methods, the Administrator shall prescribe alternative test procedures for determining compliance with the requirements of this part.

(c) The owner or operator shall permit the Administrator to conduct performance tests at any reasonable time, shall cause the affected facility to be operated for purposes of such tests under such conditions as the Administrator shall specify based on representative performance of the affected facility, and shall make available to the Administrator such records as may be necessary to determine such performance.

(d) The owner or operator of an affected facility shall provide the Administrator 10 days prior notice of the performance test to afford the Administrator the opportunity to have an observer present.

(e) The owner or operator of an affected facility shall provide, or cause to be provided, performance testing facilities as follows:

(1) Sampling ports adequate for test methods applicable to such facility.

(2) Safe sampling platform(s).

(3) Safe access to sampling platform (s).

(4) Utilities for sampling and testing equipment.

(f) Each performance test shall consist of three repetitions of the applicable test method. For the purpose of determining compliance with an applicable standard of performance, the average of results of all repetitions shall apply.

§ 60.9 Availability of information.

(a) Emission data provided to, or otherwise obtained by, the Administrator in accordance with the provisions of this part shall be available to the public.

(b) Except as provided in paragraph (a) of this section, any records, reports, or information provided to, or otherwise obtained by, the Administrator in accordance with the provisions of this part shall be available to the public, except that (1) upon a showing satisfactory to the Administrator by any person that such records, reports, or information, or particular part thereof (other than emission data), if made public, would divulge methods or processes entitled to protection as trade secrets of such person, the Administrator shall consider such records, reports, or information, or particular part thereof, confidential in accordance with the purposes of section 1905 of title 18 of the United States Code, except that such records, reports, or information, or particular part thereof, may be disclosed to other officers, employees, or authorized representatives of the United States concerned with carrying out the provisions of the Act or when relevant in any proceeding under the Act; and (2) information received by the Administrator solely for the purposes of §§ 60.5 and 60.6 shall not be disclosed if it is identified by the owner or operator as being a trade secret or commercial or financial information which such owner or operator considers confidential.

§ 60.10 State authority.

The provisions of this part shall not be construed in any manner to preclude any State or political subdivision thereof from:

(a) Adopting and enforcing any emission standard or limitation applicable to an affected facility, provided that such emission standard or limitation is not less stringent than the standard applicable to such facility.

(b) Requiring the owner or operator of an affected facility to obtain permits, licenses, or approvals prior to initiating construction, modification, or operation of such facility.

Subpart D—Standards of Performance for Fossil-Fuel Fired Steam Generators

§ 60.40 Applicability and designation of affected facility.

The provisions of this subpart are applicable to each fossil fuel-fired steam generating unit of more than 250 million B.t.u. per hour heat input, which is the affected facility.

§ 60.41 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act, and in Subpart A of this part.

(a) "Fossil fuel-fired steam generating unit" means a furnace or boiler used in the process of burning fossil fuel for the primary purpose of producing steam by heat transfer.

(b) "Fossil fuel" means natural gas, petroleum, coal and any form of solid, liquid, or gaseous fuel derived from such materials.

(c) "Particulate matter" means any finely divided liquid or solid material, other than uncombined water, as measured by Method 5.

§ 60.42 Standard for particulate matter.

On and after the date on which the performance test required to be conducted by § 60.8 is initiated no owner or operator subject to the provisions of this part shall discharge or cause the discharge into the atmosphere of particulate matter which is:

(a) In excess of 0.10 lb. per million B.t.u. heat input (0.18 g. per million cal.) maximum 2-hour average.

(b) Greater than 20 percent opacity, except that 40 percent opacity shall be permissible for not more than 2 minutes in any hour.

(c) Where the presence of uncombined water is the only reason for failure to meet the requirements of paragraph (b) of this section such failure shall not be a violation of this section.

§ 60.43 Standard for sulfur dioxide.

On and after the date on which the performance test required to be conducted by § 60.8 is initiated no owner or operator subject to the provisions of this part shall discharge or cause the discharge into the atmosphere of sulfur dioxide in excess of:

(a) 0.80 lb. per million B.t.u. heat input (1.4 g. per million cal.), maximum 2-hour average, when liquid fossil fuel is burned.

(b) 1.2 lbs. per million B.t.u. heat input (2.2 g. per million cal.), maximum 2-hour average, when solid fossil fuel is burned.

(c) Where different fossil fuels are burned simultaneously in any combination, the applicable standard shall be determined by proration. Compliance shall be determined using the following formula:

$$\frac{y(0.80)+z(1.2)}{x+y+z}$$

where:

x is the percent of total heat input derived from gaseous fossil fuel and,
y is the percent of total heat input derived from liquid fossil fuel and,
z is the percent of total heat input derived from solid fossil fuel.

§ 60.44 Standard for nitrogen oxides.

On and after the date on which the performance test required to be conducted by § 60.8 is initiated no owner or operator subject to the provisions of this part shall discharge or cause the discharge into the atmosphere of nitrogen oxides in excess of:

(a) 0.20 lb. per million B.t.u. heat input (0.36 g. per million cal.), maximum 2-hour average, expressed as NO_2, when gaseous fossil fuel is burned.

(b) 0.30 lb. per million B.t.u. heat input (0.54 g. per million cal.), maximum 2-hour average, expressed as NO_2, when liquid fossil fuel is burned.

(c) 0.70 lb. per million B.t.u. heat input (1.26 g. per million cal.), maximum 2-hour average, expressed as NO_2 when solid fossil fuel (except lignite) is burned.

(d) When different fossil fuels are burned simultaneously in any combination the applicable standard shall be determined by proration. Compliance shall be determined by using the following formula:

$$\frac{x(0.20)+y(0.30)+z(0.70)}{x+y+z}$$

where:

x is the percent of total heat input derived from gaseous fossil fuel and,
y is the percent of total heat input derived from liquid fossil fuel and,
z is the percent of total heat input derived from solid fossil fuel.

§ 60.45 Emission and fuel monitoring.

(a) There shall be installed, calibrated, maintained, and operated, in any fossil fuel-fired steam generating unit subject to the provisions of this part, emission monitoring instruments as follows:

(1) A photoelectric or other type smoke detector and recorder, except where gaseous fuel is the only fuel burned.

(2) An instrument for continuously monitoring and recording sulfur dioxide emissions, except where gaseous fuel is the only fuel burned, or where compliance is achieved through low sulfur fuels and representative sulfur analysis of fuels are conducted daily in accordance with paragraph (c) or (d) of this section.

(3) An instrument for continuously monitoring and recording emissions of nitrogen oxides.

(b) Instruments and sampling systems installed and used pursuant to this section shall be capable of monitoring emission levels within ±20 percent with a confidence level of 95 percent and shall be calibrated in accordance with the method(s) prescribed by the manufacturer(s) of such instruments; instruments shall be subjected to manufacturers recommended zero adjustment and calibration procedures at least once per 24-hour operating period unless the manufacturer(s) specifies or recommends calibration at shorter intervals, in which case such specifications or recommendations shall be followed. The applicable method specified in the appendix of this part shall be the reference method.

(c) The sulfur content of solid fuels, as burned, shall be determined in accordance with the following methods of the American Society for Testing and Materials.

(1) Mechanical sampling by Method D 2234065.

(2) Sample preparation by Method D 2013–65.

(3) Sample analysis by Method D 271–68.

(d) The sulfur content of liquid fuels, as burned, shall be determined in accordance with the American Society for Testing and Materials Methods D 1551–68, or D 129–64, or D 1552–64.

(e) The rate of fuel burned for each fuel shall be measured daily or at shorter intervals and recorded. The heating value and ash content of fuels shall be ascertained at least once per week and recorded. Where the steam generating unit is used to generate electricity, the average electrical output and the minimum and maximum hourly generation rate shall be measured and recorded daily.

(f) The owner or operator of any fossil fuel-fired steam generating unit subject to the provisions of this part shall maintain a file of all measurements required by this part. Appropriate measurements shall be reduced to the units of the applicable standard daily, and summarized monthly. The record of any such measurement(s) and summary shall be retained for at least 2 years following the date of such measurements and summaries.

§ 60.46 Test methods and procedures.

(a) The provisions of this section are applicable to performance tests for determining emissions of particulate matter, sulfur dioxide, and nitrogen oxides from fossil fuel-fired steam generating units.

(b) All performance tests shall be conducted while the affected facility is operating at or above the maximum steam production rate at which such facility will be operated and while fuels or combinations of fuels representative of normal operation are being burned and under such other relevant conditions as the Administrator shall specify based on representative performance of the affected facility.

(c) Test methods set forth in the appendix to this part or equivalent methods approved by the Administrator shall be used as follows:

(1) For each repetition, the average concentration of particulate matter shall be determined by using Method 5. Traversing during sampling by Method 5 shall be according to Method 1. The minimum sampling time shall be 2 hours, and minimum sampling volume shall be 60 $ft.^3$ corrected to standard conditions on a dry basis.

(2) For each repetition, the SO_2 concentration shall be determined by using Method 6. The sampling site shall be the same as for determining volumetric flow rate. The sampling point in the duct shall be at the centroid of the cross section if the cross sectional area is less than 50 $ft.^2$ or at a point no closer to the walls than 3 feet if the cross sectional area is 50 $ft.^2$ or more. The sample shall be extracted at a rate proportional to the gas velocity at the sampling point. The minimum sampling time shall be 20 min. and minimum sampling volume shall be 0.75 $ft.^3$ corrected to standard conditions. Two samples shall constitute one repetition and shall be taken at 1-hour intervals.

(3) For each repetition the NO_x concentration shall be determined by using Method 7. The sampling site and point shall be the same as for SO_2. The sampling time shall be 2 hours, and four samples shall be taken at 30-minute intervals.

(4) The volumetric flow rate of the total effluent shall be determined by using Method 2 and traversing according to Method 1. Gas analysis shall be performed by Method 3, and moisture content shall be determined by the condenser technique of Method 5.

(d) Heat input, expressed in B.t.u. per hour, shall be determined during each 2-hour testing period by suitable fuel flow meters and shall be confirmed by a material balance over the steam generation system.

(e) For each repetition, emissions, expressed in lb./10^6 B.t.u. shall be determined by dividing the emission rate in lb./hr. by the heat input. The emission rate shall be determined by the equation, lb./hr.$=Q_s\times c$ where, $Q_s=$volumetric flow rate of the total effluent in $ft.^3$/hr. at standard conditions, dry basis, as determined in accordance with paragraph (c)(4) of this section.

(1) For particulate matter, c=particulate concentration in lb./$ft.^3$, as determined in accordance with paragraph (c)(1) of this section, corrected to standard conditions, dry basis

(2) For SO_2, c=SO_2 concentration in lb./ft.^{3}, as determined in accordance with paragraph (c)(2) of this section, corrected to standard conditions, dry basis;

(3) For NO_x, c=NO_x concentration in lb./ft.^{3}, as determined in accordance with paragraph (c)(3) of this section, corrected to standard conditions, dry basis.

Subpart E—Standards of Performance for Incinerators

§ 60.50 Applicability and designation of affected facility.

The provisions of this subpart are applicable to each incinerator of more than 50 tons per day charging rate, which is the affected facility.

§ 60.51 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act and in Subpart A of this part.

(a) "Incinerator" means any furnace used in the process of burning solid waste for the primary purpose of reducing the volume of the waste by removing combustible matter.

(b) "Solid waste" means refuse, more than 50 percent of which is municipal type waste consisting of a mixture of paper, wood, yard wastes, food wastes, plastics, leather, rubber, and other combustibles, and noncombustible materials such as glass and rock.

(c) "Day" means 24 hours.

(d) "Particulate matter" means any finely divided liquid or solid material, other than uncombined water, as measured by Method 5.

§ 60.52 Standard for particulate matter.

On and after the date on which the performance test required to be conducted by § 60.8 is initiated, no owner or operator subject to the provisions of this part shall discharge or cause the discharge into the atmosphere of particulate matter which is in excess of 0.08 gr./s.c.f. (0.18 g./NM^3) corrected to 12 percent CO_2, maximum 2-hour average.

§ 60.53 Monitoring of operations.

The owner or operator of any incinerator subject to the provisions of this part shall maintain a file of daily burning rates and hours of operation and any particulate emission measurements. The burning rates and hours of operation shall be summarized monthly. The record(s) and summary shall be retained for at least 2 years following the date of such records and summaries.

§ 60.54 Test methods and procedures.

(a) The provisions of this section are applicable to performance tests for determining emissions of particulate matter from incinerators.

(b) All performance tests shall be conducted while the affected facility is operating at or above the maximum refuse charging rate at which such facility will be operated and the solid waste burned shall be representative of normal operation and under such other relevant conditions as the Administrator shall specify based on representative performance of the affected facility.

(c) Test methods set forth in the appendix to this part or equivalent methods approved by the Administrator shall be used as follows:

(1) For each repetition, the average concentration of particulate matter shall be determined by using Method 5. Traversing during sampling by Method 5 shall be according to Method 1. The minimum sampling time shall be 2 hours and the minimum sampling volume shall be 60 ft.^{3} corrected to standard conditions on a dry basis.

(2) Gas analysis shall be performed using the integrated sample technique of Method 3, and moisture content shall be determined by the condenser technique of Method 5. If a wet scrubber is used, the gas analysis sample shall reflect flue gas conditions after the scrubber, allowing for the effect of carbon dioxide absorption.

(d) For each repetition particulate matter emissions, expressed in gr./s.c.f., shall be determined in accordance with paragraph (c)(1) of this section corrected to 12 percent CO_2, dry basis.

Subpart F—Standards of Performance for Portland Cement Plants

§ 60.60 Applicability and designation of affected facility.

The provisions of the subpart are applicable to the following affected facilities in portland cement plants: kiln, clinker cooler, raw mill system, finish mill system, raw mill dryer, raw material storage, clinker storage, finished product storage, conveyor transfer points, bagging and bulk loading and unloading systems.

§ 60.61 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act and in Subpart A of this part.

(a) "Portland cement plant" means any facility manufacturing portland cement by either the wet or dry process.

(b) "Particulate matter" means any finely divided liquid or solid material, other than uncombined water, as measured by Method 5.

§ 60.62 Standard for particulate matter.

(a) On and after the date on which the performance test required to be conducted by § 60.8 is initiated no owner or operator subject to the provisions of this part shall discharge or cause the discharge into the atmosphere of particulate matter from the kiln which is:

(1) In excess of 0.30 lb. per ton of feed to the kiln (0.15 Kg. per metric ton), maximum 2-hour average.

(2) Greater than 10 percent opacity, except that where the presence of uncombined water is the only reason for failure to meet the requirements for this subparagraph, such failure shall not be a violation of this section.

(b) On and after the date on which the performance test required to be conducted by § 60.8 is initiated no owner or operator subject to the provisions of this part shall discharge or cause the discharge into the atmosphere of particulate matter from the clinker cooler which is:

(1) In excess of 0.10 lb. per ton of feed to the kiln (0.050 Kg. per metric ton) maximum 2-hour average.

(2) 10 percent opacity or greater.

(c) On and after the date on which the performance test required to be conducted by § 60.8 is initiated no owner or operator subject to the provisions of this part shall discharge or cause the discharge into the atmosphere of particulate matter from any affected facility other than the kiln and clinker cooler which is 10 percent opacity or greater.

§ 60.63 Monitoring of operations.

The owner or operator of any portland cement plant subject to the provisions of this part shall maintain a file of daily production rates and kiln feed rates and any particulate emission measurements. The production and feed rates shall be summarized monthly. The record(s) and summary shall be retained for at least 2 years following the date of such records and summaries.

§ 60.64 Test methods and procedures.

(a) The provisions of this section are applicable to performance tests for determining emissions of particulate matter from portland cement plant kilns and clinker coolers.

(b) All performance tests shall be conducted while the affected facility is operating at or above the maximum production rate at which such facility will be operated and under such other relevant conditions as the Administrator shall specify based on representative performance of the affected facility.

(c) Test methods set forth in the appendix to this part or equivalent methods approved by the Administrator shall be used as follows:

(1) For each repetition, the average concentration of particulate matter shall be determined by using Method 5. Traversing during sampling by Method 5 shall be according to Method 1. The minimum sampling time shall be 2 hours and the minimum sampling volume shall be 60 ft.^{3} corrected to standard conditions on a dry basis.

(2) The volumetric flow rate of the total effluent shall be determined by using Method 2 and traversing according to Method 1. Gas analysis shall be performed using the integrated sample technique of Method 3, and moisture content shall be determined by the condenser technique of Method 5.

(d) Total kiln feed (except fuels), expressed in tons per hour on a dry basis, shall be determined during each 2-hour testing period by suitable flow meters and shall be confirmed by a material balance over the production system.

(e) For each repetition, particulate matter emissions, expressed in lb./ton of kiln feed shall be determined by dividing the emission rate in lb./hr. by the kiln feed. The emission rate shall be determined by the equation, lb./hr.=$Q_s \times c$, where Q_s=volumetric flow rate of the total effluent in ft.^{3}/hr. at standard conditions, dry basis, as determined in accordance with paragraph (c)(2) of this section, and, c=particulate concentration in lb./ft.^{3}, as determined in accordance with paragraph (c)(1) of this section, corrected to standard conditions, dry basis.

Subpart G—Standards of Performance for Nitric Acid Plants

§ 60.70 Applicability and designation of affected facility.

The provisions of this subpart are applicable to each nitric acid production unit, which is the affected facility.

§ 60.71 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act and in Subpart A of this part.

(a) "Nitric acid production unit" means any facility producing weak nitric acid by either the pressure or atmospheric pressure process.

(b) "Weak nitric acid" means acid which is 30 to 70 percent in strength.

§ 60.72 Standard for nitrogen oxides.

On and after the date on which the performance test required to be conducted by § 60.8 is initiated no owner or operator subject to the provisions of this part shall discharge or cause the discharge into the atmosphere of nitrogen oxides which are:

(a) In excess of 3 lbs. per ton of acid produced (1.5 kg. per metric ton), maximum 2-hour average, expressed as NO_2.

(b) 10 percent opacity or greater.

§ 60.73 Emission monitoring.

(a) There shall be installed, calibrated, maintained, and operated, in any nitric acid production unit subject to the provisions of this subpart, an instrument for continuously monitoring and recording emissions of nitrogen oxides.

(b) The instrument and sampling system installed and used pursuant to this section shall be capable of monitoring emission levels within ±20 percent with a confidence level of 95 percent and shall be calibrated in accordance with the method(s) prescribed by the manufacturer(s) of such instrument, the instrument shall be subjected to manufacturers recommended zero adjustment and calibration procedures at least once per 24-hour operating period unless the manufacturer(s) specifies or recommends calibration at shorter intervals, in which case such specifications or recommendations shall be followed. The applicable method specified in the appendix of this part shall be the reference method.

(c) Production rate and hours of operation shall be recorded daily.

(d) The owner or operator of any nitric acid production unit subject to the provisions of this part shall maintain a file of all measurements required by this subpart. Appropriate measurements shall be reduced to the units of the standard daily and summarized monthly. The record of any such measurement and summary shall be retained for at least 2 years following the date of such measurements and summaries.

§ 60.74 Test methods and procedures.

(a) The provisions of this section are applicable to performance tests for determining emissions of nitrogen oxides from nitric acid production units.

(b) All performance tests shall be conducted while the affected facility is operating at or above the maximum acid production rate at which such facility will be operated and under such other relevant conditions as the Administrator shall specify based on representative performance of the affected facility.

(c) Test methods set forth in the appendix to this part or equivalent methods as approved by the Administrator shall be used as follows:

(1) For each repetition the NO_x concentration shall be determined by using Method 7. The sampling site shall be selected according to Method 1 and the sampling point shall be the centroid of the stack or duct. The sampling time shall be 2 hours and four samples shall be taken at 30-minute intervals.

(2) The volumetric flow rate of the total effluent shall be determined by using Method 2 and traversing according to Method 1. Gas analysis shall be performed by using the integrated sample technique of Method 3, and moisture content shall be determined by Method 4.

(d) Acid produced, expressed in tons per hour of 100 percent nitric acid, shall be determined during each 2-hour testing period by suitable flow meters and shall be confirmed by a material balance over the production system.

(e) For each repetition, nitrogen oxides emissions, expressed in lb./ton of 100 percent nitric acid, shall be determined by dividing the emission rate in lb./hr. by the acid produced. The emission rate shall be determined by the equation, lb./hr.=$Q_s \times c$, where Q_s=volumetric flow rate of the effluent in ft.^{3}/hr. at standard conditions, dry basis, as determined in accordance with paragraph (c)(2) of this section, and c=NO_x concentration in lb./ft.^{3}, as determined in accordance with paragraph (c)(1) of this section, corrected to standard conditions, dry basis.

Subpart H—Standards of Performance for Sulfuric Acid Plants

§ 60.80 Applicability and designation of affected facility.

The provisions of this subpart are applicable to each sulfuric acid production unit, which is the affected facility.

§ 60.81 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act and in Subpart A of this part.

(a) "Sulfuric acid production unit" means any facility producing sulfuric acid by the contact process by burning elemental sulfur, alkylation acid, hydrogen sulfide, organic sulfides and mercaptans, or acid sludge, but does not include facilities where conversion to sulfuric acid is utilized primarily as a means of preventing emissions to the atmosphere of sulfur dioxide or other sulfur compounds.

(b) "Acid mist" means sulfuric acid mist, as measured by test methods set forth in this part.

§ 60.82 Standard for sulfur dioxide.

On and after the date on which the performance test required to be conducted by § 60.8 is initiated no owner or operator subject to the provisions of this part shall discharge or cause the discharge into the atmosphere of sulfur dioxide in excess of 4 lbs. per ton of acid produced (2 kg. per metric ton), maximum 2-hour average.

§ 60.83 Standard for acid mist.

On and after the date on which the performance test required to be conducted by § 60.8 is initiated no owner or operator subject to the provisions of this part shall discharge or cause the discharge into the atmosphere of acid mist which is:

(a) In excess of 0.15 lb. per ton of acid produced (0.075 kg. per metric ton), maximum 2-hour average, expressed as H_2SO_4.

(b) 10 percent opacity or greater.

§ 60.84 Emission monitoring.

(a) There shall be installed, calibrated, maintained, and operated, in any sulfuric acid production unit subject to the provisions of this subpart, an instrument for continuously monitoring and recording emissions of sulfur dioxide.

(b) The instrument and sampling system installed and used pursuant to this section shall be capable of monitoring emission levels within ±20 percent with a confidence level of 95 percent and shall be calibrated in accordance with the method(s) prescribed by the manufacturer(s) of such instrument, the instrument shall be subject to manufacturers recommended zero adjustment calibration procedures at least once per 24-hour operating period unless the manufacturer(s) specified or recommends calibration at shorter intervals, in which case such specifications or recommendations shall be followed. The applicable method specified in the appendix of this part shall be the reference method.

(c) Production rate and hours of operation shall be recorded daily.

(d) The owner or operator of any sulfuric acid production unit subject to the provisions of this subpart shall maintain a file of all measurements required by this subpart. Appropriate measurements shall be reduced to the units of the applicable standard daily and summarized monthly. The record of any such measurement and summary shall be retained for at least 2 years following the date of such measurements and summaries.

§ 60.85 Test methods and procedures.

(a) The provisions of this section are applicable to performance tests for determining emissions of acid mist and sulfur dioxide from sulfuric acid production units.

(b) All performance tests shall be conducted while the affected facility is operating at or above the maximum acid production rate at which such facility will be operated and under such other relevant conditions as the Administrator shall specify based on representative performance of the affected facility.

(c) Test methods set forth in the appendix to this part or equivalent methods as approved by the Administrator shall be used as follows:

(1) For each repetition the acid mist and SO_2 concentrations shall be determined by using Method 8 and traversing according to Method 1. The minimum sampling time shall be 2 hours, and minimum sampling volume shall be 40 $ft.^3$ corrected to standard conditions.

(2) The volumetric flow rate of the total effluent shall be determined by using Method 2 and traversing according to Method 1. Gas analysis shall be performed by using the integrated sample technique of Method 3. Moisture content can be considered to be zero.

(d) Acid produced, expressed in tons per hour of 100 percent sulfuric acid shall be determined during each 2-hour testing period by suitable flow meters and shall be confirmed by a material balance over the production system.

(e) For each repetition acid mist and sulfur dioxide emissions, expressed in lb./ton of 100 percent sulfuric acid shall be determined by dividing the emission rate in lb./hr. by the acid produced. The emission rate shall be determined by the equation, lb./hr.$=Q_s \times c$, where Q_s=volumetric flow rate of the effluent in $ft.^3$/hr. at standard conditions, dry basis as determined in accordance with paragraph (c)(2) of this section, and c=acid mist and SO_2 concentrations in lb./$ft.^3$ as determined in accordance with paragraph (c)(1) of this section, corrected to standard conditions, dry basis.

APPENDIX—TEST METHODS

METHOD 1—SAMPLE AND VELOCITY TRAVERSES FOR STATIONARY SOURCES

1. *Principle and Applicability.*

1.1 Principle. A sampling site and the number of traverse points are selected to aid in the extraction of a representative sample.

1.2 Applicability. This method should be applied only when specified by the test procedures for determining compliance with the New Source Performance Standards. Unless otherwise specified, this method is not intended to apply to gas streams other than those emitted directly to the atmosphere without further processing.

2. *Procedure.*

2.1 Selection of a sampling site and minimum number of traverse points.

2.1.1 Select a sampling site that is at least eight stack or duct diameters downstream and two diameters upstream from any flow disturbance such as a bend, expansion, contraction, or visible flame. For rectangular cross section, determine an equivalent diameter from the following equation:

$$\text{equivalent diameter}=2\left(\frac{(\text{length})(\text{width})}{\text{length}+\text{width}}\right)$$

equation 1-1

2.1.2 When the above sampling site criteria can be met, the minimum number of traverse points is twelve (12).

2.1.3 Some sampling situations render the above sampling site criteria impractical. When this is the case, choose a convenient sampling location and use Figure 1-1 to determine the minimum number of traverse points. Under no conditions should a sampling point be selected within 1 inch of the stack wall. To obtain the number of traverse points for stacks or ducts with a diameter less than 2 feet, multiply the number of points obtained from Figure 1-1 by 0.67.

2.1.4 To use Figure 1-1 first measure the distance from the chosen sampling location to the nearest upstream and downstream disturbances. Determine the corresponding number of traverse points for each distance from Figure 1-1. Select the higher of the two numbers of traverse points, or a greater value, such that for circular stacks the number is a multiple of 4, and for rectangular stacks the number follows the criteria of section 2.2.2.

2.2 Cross-sectional layout and location of traverse points.

2.2.1 For circular stacks locate the traverse points on at least two diameters according to Figure 1-2 and Table 1-1. The traverse axes shall divide the stack cross section into equal parts.

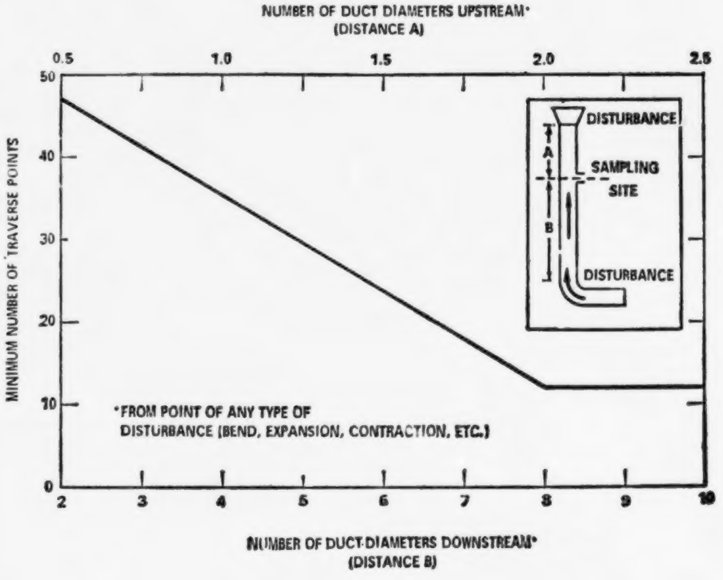

Figure 1-1. Minimum number of traverse points.

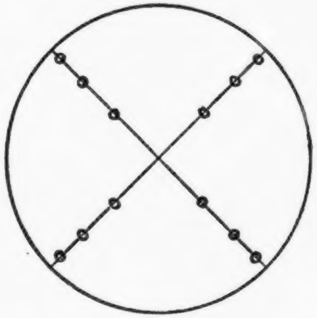

Figure 1-2. Cross section of circular stack divided into 12 equal areas, showing location of traverse points at centroid of each area.

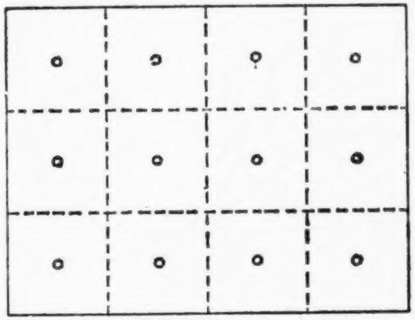

Figure 1-3. Cross section of rectangular stack divided into 12 equal areas, with traverse points at centroid of each area.

Table 1-1. Location of traverse points in circular stacks
(Percent of stack diameter from inside wall to traverse point)

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8				96.7	85.4	65.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.9	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

2.2.2 For rectangular stacks divide the cross section into as many equal rectangular areas as traverse points, such that the ratio of the length to the width of the elemental areas is between one and two. Locate the traverse points at the centroid of each equal area according to Figure 1-3.

3. *References.*

Determining Dust Concentration in a Gas Stream, ASME Performance Test Code #27, New York, N.Y., 1957.

Devorkin, Howard, et al., Air Pollution Source Testing Manual, Air Pollution Control District, Los Angeles, Calif. November 1963.

Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases, Western Precipitation Division of Joy Manufacturing Co., Los Angeles, Calif. Bulletin WP-50, 1968.

Standard Method for Sampling Stacks for Particulate Matter, In: 1971 Book of ASTM Standards, Part 23, Philadelphia, Pa. 1971, ASTM Designation D-2928-71.

METHOD 2—DETERMINATION OF STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE (TYPE S PITOT TUBE)

1. *Principle and applicability.*

1.1 Principle. Stack gas velocity is determined from the gas density and from measurement of the velocity head using a Type S (Stauscheibe or reverse type) pitot tube.

1.2 Applicability. This method should be applied only when specified by the test procedures for determining compliance with the New Source Performance Standards.

2. *Apparatus.*

2.1 Pitot tube—Type S (Figure 2-1), or equivalent, with a coefficient within ±5% over the working range.

2.2 Differential pressure gauge—Inclined manometer, or equivalent, to measure velocity head to within 10% of the minimum value.

2.3 Temperature gauge—Thermocouple or equivalent attached to the pitot tube to measure stack temperature to within 1.5% of the minimum absolute stack temperature.

2.4 Pressure gauge—Mercury-filled U-tube manometer, or equivalent, to measure stack pressure to within 0.1 in. Hg.

2.5 Barometer—To measure atmospheric pressure to within 0.1 in. Hg.

2.6 Gas analyzer—To analyze gas composition for determining molecular weight.

2.7 Pitot tube—Standard type, to calibrate Type S pitot tube.

3. *Procedure.*

3.1 Set up the apparatus as shown in Figure 2-1. Make sure all connections are tight and leak free. Measure the velocity head and temperature at the traverse points specified by Method 1.

3.2 Measure the static pressure in the stack.

3.3 Determine the stack gas molecular weight by gas analysis and appropriate calculations as indicated in Method 3.

4. *Calibration.*

4.1 To calibrate the pitot tube, measure the velocity head at some point in a flowing gas stream with both a Type S pitot tube and a standard type pitot tube with known coefficient. Calibration should be done in the laboratory and the velocity of the flowing gas stream should be varied over the normal working range. It is recommended that the calibration be repeated after use at each field site.

4.2 Calculate the pitot tube coefficient using equation 2-1.

$$C_{p_{test}} = C_{p_{std}} \sqrt{\frac{\Delta p_{std}}{\Delta p_{test}}} \quad \text{equation 2-1}$$

where:

$C_{p_{test}}$ = Pitot tube coefficient of Type S pitot tube.

$C_{p_{std}}$ = Pitot tube coefficient of standard type pitot tube (if unknown, use 0.99).

Δp_{std} = Velocity head measured by standard type pitot tube.

Δp_{test} = Velocity head measured by Type S pitot tube.

4.3 Compare the coefficients of the Type S pitot tube determined first with one leg and then the other pointed downstream. Use the pitot tube only if the two coefficients differ by no more than 0.01.

5. *Calculations.*

Use equation 2-2 to calculate the stack gas velocity.

$$(V_s)_{avg.} = K_p C_p (\sqrt{\Delta p})_{avg.} \sqrt{\frac{(T_s)_{avg.}}{P_s M_s}}$$

Equation 2-2

where:

$(V_s)_{avg}$ = Stack gas velocity, feet per second (f.p.s.).

$K_p = 85.48 \frac{ft.}{sec.} \left(\frac{lb.}{lb.\ mole\text{-}°R} \right)^{1/2}$ when these units are used.

C_p = Pitot tube coefficient, dimensionless.

$(T_s)_{avg.}$ = Average absolute stack gas temperature, °R.

$(\sqrt{\Delta p})_{avg.}$ = Average velocity head of stack gas, inches H_2O (see Fig. 2-2).

P_s = Absolute stack gas pressure, inches Hg.

M_s = Molecular weight of stack gas (wet basis), lb./lb.-mole.

$M_d(1-B_{wo})+18B_{wo}$

M_d = Dry molecular weight of stack gas (from Method 3).

B_{wo} = Proportion by volume of water vapor in the gas stream (from Method 4).

Figure 2-2 shows a sample recording sheet for velocity traverse data. Use the averages in the last two columns of Figure 2-2 to determine the average stack gas velocity from Equation 2-2.

Use Equation 2-3 to calculate the stack gas volumetric flow rate.

$$Q_s = 3600\ (1-B_{wo}) V_s A \left(\frac{T_{std}}{(T_s)_{avg.}} \right) \left(\frac{P_s}{P_{std}} \right)$$

Equation 2-3

where:

Q_s = Volumetric flow rate, dry basis, standard conditions, ft.³/hr.

A = Cross-sectional area of stack, ft.²

T_{std} = Absolute temperature at standard conditions, 530° R.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

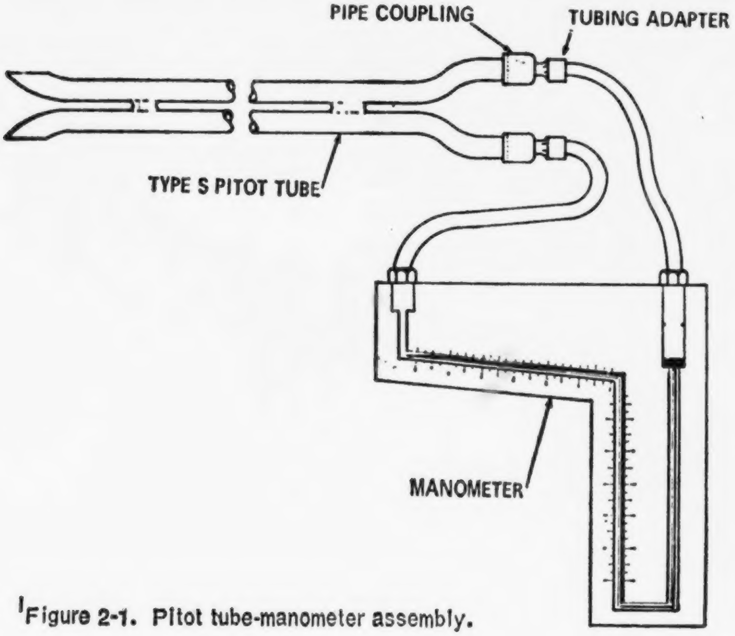

Figure 2-1. Pitot tube-manometer assembly.

6. *References.*

Mark, L. S., Mechanical Engineers' Handbook, McGraw-Hill Book Co., Inc., New York, N.Y., 1951.

Perry, J. H., Chemical Engineers' Handbook, McGraw-Hill Book Co., Inc., New York, N.Y., 1960.

Shigehara, R. T., W. F. Todd, and W. S. Smith, Significance of Errors in Stack Sampling Measurements. Paper presented at the Annual Meeting of the Air Pollution Control Association, St. Louis, Mo., June 14–19, 1970.

Standard Method for Sampling Stacks for Particulate Matter, In: 1971 Book of ASTM Standards, Part 23, Philadelphia, Pa., 1971, ASTM Designation D–2928–71.

Vennard, J. K., Elementary Fluid Mechanics, John Wiley & Sons, Inc., New York, N.Y., 1947.

PLANT____________________

DATE____________________

RUN NO.____________________

STACK DIAMETER, in.____________________

BAROMETRIC PRESSURE, in. Hg____________________

STATIC PRESSURE IN STACK (P_g), in. Hg.__________

OPERATORS____________________

SCHEMATIC OF STACK CROSS SECTION

Traverse point number	Velocity head, in. H_2O	$\sqrt{\Delta_p}$	Stack Temperature (T_S), °F
	AVERAGE:		

Figure 2-2. Velocity traverse data.

METHOD 3—GAS ANALYSIS FOR CARBON DIOXIDE, EXCESS AIR, AND DRY MOLECULAR WEIGHT

1. *Principle and applicability.*

1.1 Principle. An integrated or grab gas sample is extracted from a sampling point and analyzed for its components using an Orsat analyzer.

1.2 Applicability. This method should be applied only when specified by the test procedures for determining compliance with the New Source Performance Standards. The test procedure will indicate whether a grab sample or an integrated sample is to be used.

2. *Apparatus.*

2.1 Grab sample (Figure 3-1).

2.1.1 Probe—Stainless steel or Pyrex[1] glass, equipped with a filter to remove particulate matter.

2.1.2 Pump—One-way squeeze bulb, or equivalent, to transport gas sample to analyzer.

2.2 *Integrated sample (Figure 3-2).*

2.2.1 Probe—Stainless steel or Pyrex[1] glass, equipped with a filter to remove particulate matter.

2.2.2 Air-cooled condenser or equivalent—To remove any excess moisture.

2.2.3 Needle valve—To adjust flow rate.

2.2.4 Pump—Leak-free, diaphragm type, or equivalent, to pull gas.

2.2.5 Rate meter—To measure a flow range from 0 to 0.035 cfm.

2.2.6 Flexible bag—Tedlar,[1] or equivalent, with a capacity of 2 to 3 cu. ft. Leak test the bag in the laboratory before using.

2.2.7 Pitot tube—Type S, or equivalent, attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity when velocity is varying with time or a sample traverse is conducted.

2.3 *Analysis.*

2.3.1 Orsat analyzer, or equivalent.

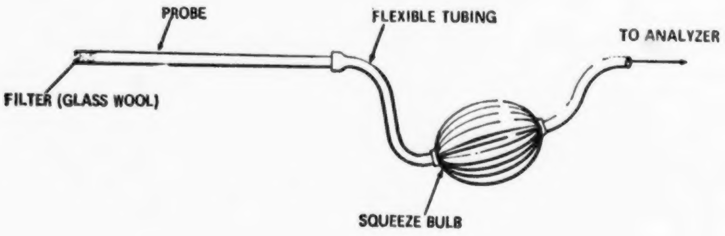

Figure 3-1. Grab-sampling train.

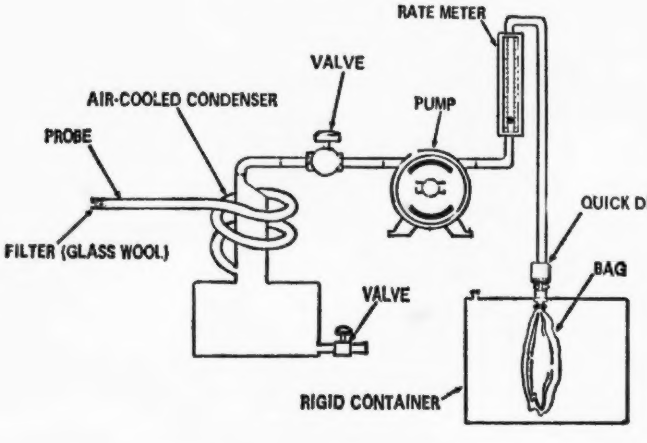

Figure 3-2. Integrated gas-sampling train.

3. *Procedure.*

3.1 Grab sampling.

3.1.1 Set up the equipment as shown in Figure 3-1, making sure all connections are leak-free. Place the probe in the stack at a sampling point and purge the sampling line.

3.1.2 Draw sample into the analyzer.

3.2 Integrated sampling.

3.2.1 Evacuate the flexible bag. Set up the equipment as shown in Figure 3-2 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are tight and that there are no leaks.

3.2.2 Sample at a rate proportional to the stack velocity.

3.3 Analysis.

3.3.1 Determine the CO_2, O_2, and CO concentrations as soon as possible. Make as many passes as are necessary to give constant readings. If more than ten passes are necessary, replace the absorbing solution.

3.3.2 For grab sampling, repeat the sampling and analysis until three consecutive samples vary no more than 0.5 percent by volume for each component being analyzed.

3.3.3 For integrated sampling, repeat the analysis of the sample until three consecutive analyses vary no more than 0.2 percent by volume for each component being analyzed.

4. *Calculations.*

4.1 Carbon dioxide. Average the three consecutive runs and report the result to the nearest 0.1% CO_2.

4.2 Excess air. Use Equation 3-1 to calculate excess air, and average the runs. Report the result to the nearest 0.1% excess air.

$$\%EA=\frac{(\%O_2)-0.5(\%CO)}{0.264(\%N_2)-(\%O_2)+0.5(\%CO)}\times 100$$

equation 3-1

where:

$\%EA$ = Percent excess air.
$\%O_2$ = Percent oxygen by volume, dry basis.
$\%N_2$ = Percent nitrogen by volume, dry basis.
$\%CO$ = Percent carbon monoxide by volume, dry basis.
0.264 = Ratio of oxygen to nitrogen in air by volume.

4.3 Dry molecular weight. Use Equation 3-2 to calculate dry molecular weight and average the runs. Report the result to the nearest tenth.

$$M_d=0.44(\%CO_2)+0.32(\%O_2)+0.28(\%N_2+\%CO)$$

equation 3-2

where:

M_d = Dry molecular weight, lb./lb-mole.
$\%CO_2$ = Percent carbon dioxide by volume, dry basis.
$\%O_2$ = Percent oxygen by volume, dry basis.
$\%N_2$ = Percent nitrogen by volume, dry basis.
0.44 = Molecular weight of carbon dioxide divided by 100.
0.32 = Molecular weight of oxygen divided by 100.
0.28 = Molecular weight of nitrogen and CO divided by 100.

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[1] Trade name.

5. *References.*

Altshuller, A. P., et al., Storage of Gases and Vapors in Plastic Bags, Int. J. Air & Water Pollution, 6:75–81, 1963.

Conner, William D., and J. S. Nader, Air Sampling with Plastic Bags, Journal of the American Industrial Hygiene Association, 25:291–297, May–June 1964.

Devorkin, Howard, et al., Air Pollution Source Testing Manual, Air Pollution Control District, Los Angeles, Calif., November 1963.

METHOD 4—DETERMINATION OF MOISTURE IN STACK GASES

1. *Principle and applicability.*

1.1 Principle. Moisture is removed from the gas stream, condensed, and determined volumetrically.

1.2 Applicability. This method is applicable for the determination of moisture in stack gas only when specified by test procedures for determining compliance with New Source Performance Standards. This method does not apply when liquid droplets are present in the gas stream[1] and the moisture is subsequently used in the determination of stack gas molecular weight.

Other methods such as drying tubes, wet bulb-dry bulb techniques, and volumetric condensation techniques may be used.

2. *Apparatus.*

2.1 Probe—Stainless steel or Pyrex[2] glass sufficiently heated to prevent condensation and equipped with a filter to remove particulate matter.

2.2 Impingers—Two midget impingers, each with 30 ml. capacity, or equivalent.

2.3 Ice bath container—To condense moisture in impingers.

2.4 Silica gel tube (optional)—To protect pump and dry gas meter.

2.5 Needle valve—To regulate gas flow rate.

2.6 Pump—Leak-free, diaphragm type, or equivalent, to pull gas through train.

2.7 Dry gas meter—To measure to within 1% of the total sample volume.

2.8 Rotameter—To measure a flow range from 0 to 0.1 c.f.m.

2.9 Graduated cylinder—25 ml.

2.10 Barometer—Sufficient to read to within 0.1 inch Hg.

2.11 Pitot tube—Type S, or equivalent, attached to probe so that the sampling flow rate can be regulated proportional to the stack gas velocity when velocity is varying with time or a sample traverse is conducted.

3. *Procedure.*

3.1 Place exactly 5 ml. distilled water in each impinger. Assemble the apparatus without the probe as shown in Figure 4–1. Leak check by plugging the inlet to the first impinger and drawing a vacuum. Insure that flow through the dry gas meter is less than 1% of the sampling rate.

3.2 Connect the probe and sample at a constant rate of 0.075 c.f.m. or at a rate proportional to the stack gas velocity. Continue sampling until the dry gas meter registers 1 cubic foot or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as required by Figure 4–2.

3.3 After collecting the sample, measure the volume increase to the nearest 0.5 ml.

4. *Calculations.*

4.1 Volume of water vapor collected.

$$V_{wc}=\frac{(V_f-V_i)\rho_{H_2O}RT_{std}}{P_{std}M_{H_2O}}=0.0474\frac{\text{ft.}^3}{\text{ml.}}(V_f-V_i) \qquad \text{equation 4-1}$$

where:

V_{wc}=Volume of water vapor collected (standard conditions), cu. ft.

V_f=Final volume of impinger contents, ml.

V_i=Initial volume of impinger contents, ml.

R=Ideal gas constant, 21.83 inches Hg—cu. ft./lb. mole-°R.

ρ_{H_2O}=Density of water, 1 g./ml.

T_{std}=Absolute temperature at standard conditions, 530° R.

P_{std}=Absolute pressure at standard conditions, 29.92 inches Hg.

M_{H_2O}=Molecular weight of water, 18 lb./lb.-mole.

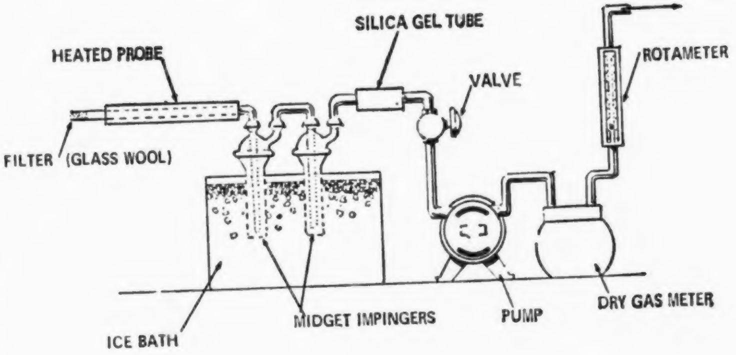

Figure 4-1. Moisture-sampling train.

LOCATION________________ COMMENTS

TEST________________

DATE________________

OPERATOR________________

BAROMETRIC PRESSURE________________

CLOCK TIME	GAS VOLUME THROUGH METER, (Vm), ft^3	ROTAMETER SETTING ft^3/min	METER TEMPERATURE, °F

Figure 4-2. Field moisture determination.

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[1] If liquid droplets are present in the gas stream, assume the stream to be saturated, determine the average stack gas temperature by traversing according to Method 1, and use a psychrometric chart to obtain an approximation of the moisture percentage.

[2] Trade name.

4.2 Gas volume.

$$V_{mc}=V_m\left(\frac{P_m}{P_{std}}\right)\left(\frac{T_{std}}{T_m}\right)= 17.71\ \frac{°R}{\text{in. Hg}}\left(\frac{V_mP_m}{T_m}\right) \quad \text{equation 4–2}$$

where:

V_{mc} = Dry gas volume through meter at standard conditions, cu. ft.

V_m = Dry gas volume measured by meter, cu. ft.

P_m = Barometric pressure at the dry gas meter, inches Hg.

P_{std} = Pressure at standard conditions, 29.92 inches Hg.

T_{std} = Absolute temperature at standard conditions, 530° R.

T_m = Absolute temperature at meter (°F + 460), °R.

4.3 Moisture content.

$$B_{wo}=\frac{V_{wc}}{V_{wc}+V_{m}}+B_{wm}=\frac{V_{wc}}{V_{wc}+V_{mc}}+(0.025) \quad \text{equation 4–3}$$

where:

B_{wo} = Proportion by volume of water vapor in the gas stream, dimensionless.

V_{wc} = Volume of water vapor collected (standard conditions), cu. ft.

V_{mc} = Dry gas volume through meter (standard conditions), cu. ft.

B_{wm} = Approximate volumetric proportion of water vapor in the gas stream leaving the impingers, 0.025.

5. *References.*

Air Pollution Engineering Manual, Danielson, J. A. (ed.), U.S. DHEW, PHS, National Center for Air Pollution Control, Cincinnati, Ohio, PHS Publication No. 999–AP–40, 1967.

Devorkin, Howard, et al., Air Pollution Source Testing Manual, Air Pollution Control District, Los Angeles, Calif., November 1963.

Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases, Western Precipitation Division of Joy Manufacturing Co., Los Angeles, Calif., Bulletin WP–50, 1968.

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and its weight is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. *Apparatus.*

2.1 Sampling train. The design specifications of the particulate sampling train used by EPA (Figure 5–1) are described in APTD–0581. Commercial models of this train are available.

2.1.1 Nozzle—Stainless steel (316) with sharp, tapered leading edge.

2.1.2 Probe—Pyrex [1] glass with a heating system capable of maintaining a minimum gas temperature of 250° F. at the exit end during sampling to prevent condensation from occurring. When length limitations (greater than about 8 ft.) are encountered at temperatures less than 600° F., Incoloy 825 [1], or equivalent, may be used. Probes for sampling gas streams at temperatures in excess of 600° F. must have been approved by the Administrator.

2.1.3 Pitot tube—Type S, or equivalent, attached to probe to monitor stack gas velocity.

2.1.4 Filter Holder—Pyrex [1] glass with heating system capable of maintaining minimum temperature of 225° F.

2.1.5 Impingers / Condenser—Four impingers connected in series with glass ball joint fittings. The first, third, and fourth impingers are of the Greenburg-Smith design, modified by replacing the tip with a ½-inch ID glass tube extending to one-half inch from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip. A condenser may be used in place of the impingers provided that the moisture content of the stack gas can still be determined.

2.1.6 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 5° F., dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume.

2.1.7 Barometer—To measure atmospheric pressure to ±0.1 inches Hg.

2.2 Sample recovery.

2.2.1 Probe brush—At least as long as probe.

2.2.2 Glass wash bottles—Two.

2.2.3 Glass sample storage containers.

2.2.4 Graduated cylinder—250 ml.

2.3 Analysis.

2.3.1 Glass weighing dishes.

2.3.2 Desiccator.

2.3.3 Analytical balance—To measure to ±0.1 mg.

2.3.4 Trip balance—300 g. capacity, to measure to ±0.05 g.

3. *Reagents.*

3.1 Sampling.

3.1.1 Filters—Glass fiber, MSA 1106 BH [1], or equivalent, numbered for identification and preweighed.

3.1.2 Silica gel—Indicating type, 6–16 mesh, dried at 175° C. (350° F.) for 2 hours.

3.1.3 Water.

3.1.4 Crushed ice.

3.2 Sample recovery.

3.2.1 Acetone—Reagent grade.

3.3 Analysis.

3.3.1 Water.

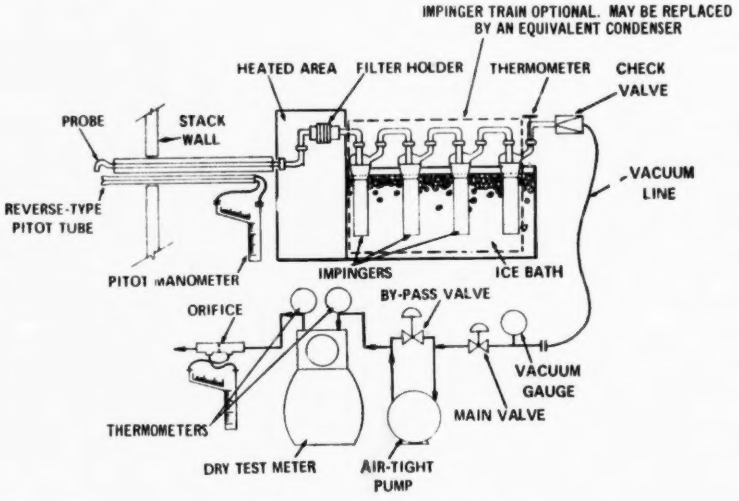

Figure 5-1. Particulate-sampling train.

3.3.2 Desiccant—Drierite,[1] indicating.

4. *Procedure.*

4.1 Sampling.

4.1.1 After selecting the sampling site and the minimum number of sampling points, determine the stack pressure, temperature, moisture, and range of velocity head.

4.1.2 Preparation of collection train. Weigh to the nearest gram approximately 200 g. of silica gel. Label a filter of proper diameter, desiccate [2] for at least 24 hours and weigh to the nearest 0.5 mg. in a room where the relative humidity is less than 50%. Place 100 ml. of water in each of the first two impingers, leave the third impinger empty, and place approximately 200 g. of preweighed silica gel in the fourth impinger. Set up the train without the probe as in Figure 5–1. Leak check the sampling train at the sampling site by plugging up the inlet to the filter holder and pulling a 15 in. Hg vacuum. A leakage rate not in excess of 0.02 c.f.m. at a vacuum of 15 in. Hg is acceptable. Attach the probe and adjust the heater to provide a gas temperature of about 250° F. at the probe outlet. Turn on the filter heating system. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger as low as possible and preferably at 70° F. or less. Temperatures above 70° F. may result in damage to the dry gas meter from either moisture condensation or excessive heat.

4.1.3 Particulate train operation. For each run, record the data required on the example sheet shown in Figure 5–2. Take readings at each sampling point, at least every 5 minutes, and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Sample for at least 5 minutes at each traverse point; sampling time must be the same for each point. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the rapid adjustment of the sampling rate without other computations. APTD–0576 details the procedure for using these nomographs. Turn off the pump at the conclusion of each run and record the final readings. Remove the probe and nozzle from the stack and handle in accordance with the sample recovery process described in section 4.2.

---

[1] Trade name.

[1] Trade name.

[2] Dry using Drierite [1] at 70° F. ±10° F.

PLANT__________
LOCATION__________
OPERATOR__________
DATE__________
RUN NO__________
SAMPLE BOX NO.__________
METER BOX NO.__________
METER ΔH@__________
C FACTOR__________

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE__________
BAROMETRIC PRESSURE__________
ASSUMED MOISTURE, %__________
HEATER BOX SETTING__________
PROBE LENGTH, m.__________
NOZZLE DIAMETER, in.__________
PROBE HEATER SETTING__________

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STATIC PRESSURE (P_s), in. Hg	STACK TEMPERATURE (T_s), °F	VELOCITY HEAD (ΔP_s),	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER (ΔH), in. H_2O	GAS SAMPLE VOLUME (V_m), ft^3	GAS SAMPLE TEMPERATURE AT DRY GAS METER		SAMPLE BOX TEMPERATURE, °F	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER °F
							INLET ($T_{m_{in}}$), °F	OUTLET ($T_{m_{out}}$), °F		
TOTAL							Avg.	Avg.		
AVERAGE							Avg.			

Figure 5-2. Particulate field data.

4.2 Sample recovery. Exercise care in moving the collection train from the test site to the sample recovery area to minimize the loss of collected sample or the gain of extraneous particulate matter. Set aside a portion of the acetone used in the sample recovery as a blank for analysis. Measure the volume of water from the first three impingers, then discard. Place the samples in containers as follows:

Container No. 1. Remove the filter from its holder, place in this container, and seal.

Container No. 2. Place loose particulate matter and acetone washings from all sample-exposed surfaces prior to the filter in this container and seal. Use a razor blade, brush, or rubber policeman to lose adhering particles.

Container No. 3. Transfer the silica gel from the fourth impinger to the original container and seal. Use a rubber policeman as an aid in removing silica gel from the impinger.

4.3 Analysis. Record the data required on the example sheet shown in Figure 5-3. Handle each sample container as follows:

Container No. 1. Transfer the filter and any loose particulate matter from the sample container to a tared glass weighing dish, desiccate, and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 2 Transfer the acetone washings to a tared beaker and evaporate to dryness at ambient temperature and pressure. Desiccate and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 3. Weigh the spent silica gel and report to the nearest gram.

5. *Calibration*.

Use methods and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, dry gas meter, and probe heater. Recalibrate after each test series.

6. *Calculations*.

6.1 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.2 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (70° F., 29.92 inches Hg) by using Equation 5-1.

$$V_{m_{std}} = V_m\left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{P_{std}}\right) = \left(17.71\,\frac{°R}{\text{in. Hg}}\right)V_m\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{T_m}\right)$$

equation 5-1

where:

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} = Absolute temperature at standard conditions, 530° R.

T_m = Average dry gas meter temperature, °R.

P_{bar} = Barometric pressure at the orifice meter, inches Hg.

ΔH = Average pressure drop across the orifice meter, inches H_2O.

13.6 = Specific gravity of mercury.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.3 Volume of water vapor.

$$V_{w_{std}} = V_{l_c}\left(\frac{\rho_{H_2O}}{M_{H_2O}}\right)\left(\frac{RT_{std}}{P_{std}}\right) = \left(0.0474\,\frac{\text{cu. ft.}}{\text{ml.}}\right)V_{l_c}$$

equation 5-2

where:

$V_{w_{std}}$ = Volume of water vapor in the gas sample (standard conditions), cu. ft.

V_{l_c} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.

ρ_{H_2O} = Density of water, 1 g./ml.

M_{H_2O} = Molecular weight of water, 18 lb./lb.-mole.

R = Ideal gas constant, 21.83 inches Hg—cu. ft./lb.-mole-°R.

T_{std} = Absolute temperature at standard conditions, 530° R.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.4 Moisture content.

$$B_{wo} = \frac{V_{w_{std}}}{V_{m_{std}} + V_{w_{std}}}$$

equation 5-3

where:

B_{wo} = Proportion by volume of water vapor in the gas stream, dimensionless.

$V_{w_{std}}$ = Volume of water in the gas sample (standard conditions), cu. ft.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

6.5 Total particulate weight. Determine the total particulate catch from the sum of the weights on the analysis data sheet (Figure 5-3).

6.6 Concentration.

6.6.1 Concentration in gr./s.c.f.

$$c'_s = \left(0.0154\,\frac{\text{gr.}}{\text{mg.}}\right)\left(\frac{M_n}{V_{m_{std}}}\right)$$

equation 5-4

where:

c'_s = Concentration of particulate matter in stack gas, gr./s.c.f., dry basis.

M_n = Total amount of particulate matter collected, mg.

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

PLANT____________________

DATE____________________

RUN NO.____________________

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL	☒	☒	

	VOLUME OF LIQUID WATER COLLECTED		
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g	
FINAL			
INITIAL			
LIQUID COLLECTED			
TOTAL VOLUME COLLECTED		g*	ml

CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER. (1 g. ml):

$$\frac{\text{INCREASE, g}}{(1\ \text{g/ml})} = \text{VOLUME WATER, ml}$$

Figure 5-3. Analytical data.

6.6.2 Concentration in lb./cu. ft.

$$c_s = \frac{\left(\frac{1}{453{,}600}\frac{\text{lb.}}{\text{mg.}}\right)M_n}{V_{m_{std}}} = 2.205\times 10^{-6}\frac{M_n}{V_{m_{std}}} \qquad \text{equation 5-5}$$

where:

c_s = Concentration of particulate matter in stack gas, lb./s.c.f., dry basis.

453,600 = Mg./lb.

M_n = Total amount of particulate matter collected, mg.

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

6.7 Isokinetic variation.

$$I = \frac{T_s\left[\frac{V_{l_c}(\rho_{H_2O})R}{M_{H_2O}} + \frac{V_m}{T_m}\left(P_{bar}+\frac{\Delta H}{13.6}\right)\right]}{\theta V_s P_s A_n}\times 100$$

$$= \frac{\left(1.667\frac{\text{min.}}{\text{sec.}}\right)\left[\left(0.00267\frac{\text{in. Hg-cu. ft.}}{\text{ml.-°R}}\right)V_{l_c} + \frac{V_m}{T_m}\left(P_{bar}+\frac{\Delta H}{13.6}\right)\right]}{\theta V_s P_s A_n} \qquad \text{Equation 5-6}$$

where:

I = Percent of isokinetic sampling.

V_{l_c} = Total volume of liquid collected in impingers and silica gel (See Fig. 5-3), ml.

ρ_{H_2O} = Density of water, 1 g./ml.

R = Ideal gas constant, 21.83 inches Hg-cu. ft./lb.-mole-°R.

M_{H_2O} = Molecular weight of water, 18 lb./lb.-mole.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_m = Absolute average dry gas meter temperature (see Figure 5-2), °R.

P_{bar} = Barometric pressure at sampling site, inches Hg.

ΔH = Average pressure drop across the orifice (see Fig. 5-2), inches H_2O.

T_s = Absolute average stack gas temperature (see Fig. 5-2), °R.

θ = Total sampling time, min.

V_s = Stack gas velocity calculated by Method 2, Equation 2-2, ft./sec.

P_s = Absolute stack gas pressure, inches Hg.

A_n = Cross-sectional area of nozzle, sq. ft.

6.8 Acceptable results. The following range sets the limit on acceptable isokinetic sampling results:

If $90\% \leq I \leq 110\%$, the results are acceptable, otherwise, reject the results and repeat the test.

7. *Reference.*

Addendum to Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, Dec. 6, 1967.

Martin, Robert M., Construction Details of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0581.

Rom, Jerome J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0576.

Smith, W. S., R. T. Shigehara, and W. F. Todd, A Method of Interpreting Stack Sampling Data, Paper presented at the 63d Annual Meeting of the Air Pollution Control Association, St. Louis, Mo., June 14-19, 1970.

Smith, W. S., et al., Stack Gas Sampling Improved and Simplified with New Equipment, APCA paper No. 67-119, 1967.

Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, 1967.

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. A gas sample is extracted from the sampling point in the stack. The acid mist, including sulfur trioxide, is separated from the sulfur dioxide. The sulfur dioxide fraction is measured by the barium-thorin titration method.

1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. *Apparatus.*

2.1 Sampling. See Figure 6-1.

2.1.1 Probe—Pyrex[1] glass, approximately 5 to 6 mm. ID, with a heating system to prevent condensation and a filtering medium to remove particulate matter including sulfuric acid mist.

2.1.2 Midget bubbler—One, with glass wool packed in top to prevent sulfuric acid mist carryover.

2.1.3 Glass wool.

2.1.4 Midget impingers—Three.

2.1.5 Drying tube—Packed with 6 to 16 mesh indicating-type silica gel, or equivalent, to dry the sample.

2.1.6 Valve—Needle valve, or equivalent, to adjust flow rate.

2.1.7 Pump—Leak-free, vacuum type.

2.1.8 Rate meter—Rotameter or equivalent, to measure a 0-10 s.c.f.h. flow range.

2.1.9 Dry gas meter—Sufficiently accurate to measure the sample volume within 1%.

2.1.10 Pitot tube—Type S, or equivalent.

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[1] Trade names.

necessary only if a sample traverse is required, or if stack gas velocity varies with time.

2.2 Sample recovery.

2.2.1 Glass wash bottles—Two.

2.2.2 Polyethylene storage bottles—To store impinger samples.

2.3 Analysis.

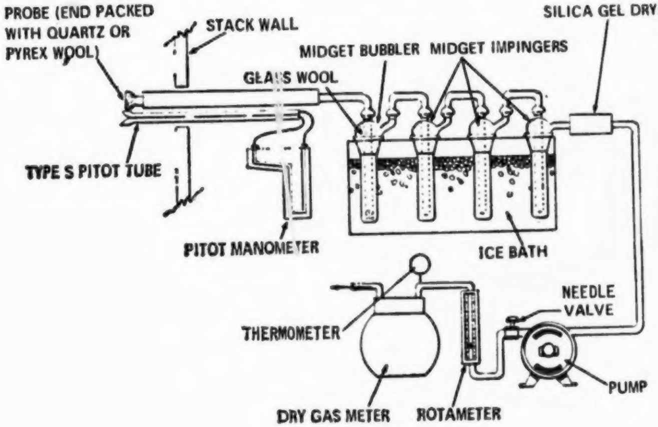

Figure 6-1. SO_2 sampling train.

2.3.1 Pipettes—Transfer type, 5 ml. and 10 ml. sizes (0.1 ml. divisions) and 25 ml. size (0.2 ml. divisions).

2.3.2 Volumetric flasks—50 ml., 100 ml., and 1,000 ml.

2.3.3 Burettes—5 ml. and 50 ml.

2.3.4 Erlenmeyer flask—125 ml.

3. *Reagents.*

3.1 Sampling.

3.1.1 Water—Deionized, distilled.

3.1.2 Isopropanol, 80%—Mix 80 ml. of isopropanol with 20 ml. of distilled water.

3.1.3 Hydrogen peroxide, 3%—dilute 100 ml. of 30% hydrogen peroxide to 1 liter with distilled water. Prepare fresh daily.

3.2 Sample recovery.

3.2.1 Water—Deionized, distilled.

3.2.2 Isopropanol, 80%.

3.3 Analysis.

3.3.1 Water—Deionized, distilled.

3.3.2 Isopropanol.

3.3.3 Thorin indicator—1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt (or equivalent). Dissolve 0.20 g. in 100 ml. distilled water.

3.3.4 Barium perchlorate (0.01 N)—Dissolve 1.95 g. of barium perchlorate $[Ba(ClO_4)_2 \cdot 3H_2O]$ in 200 ml. distilled water and dilute to 1 liter with isopropanol. Standardize with sulfuric acid. Barium chloride may be used.

3.3.5 Sulfuric acid standard (0.01 N)—Purchase or standardize to ±0.0002 N against 0.01N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

4. *Procedure.*

4.1 Sampling.

4.1.1 Preparation of collection train. Pour 15 ml. of 80% isopropanol into the midget bubbler and 15 ml. of 3% hydrogen peroxide into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6-1. Leak check the sampling train at the sampling site by plugging the probe inlet and pulling a 10 inches Hg vacuum. A leakage rate not in excess of 1% of the sampling rate is acceptable. Carefully release the probe inlet plug and turn off the pump. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 70° F. or less.

4.1.2 Sample collection. Adjust the sample flow rate proportional to the stack gas velocity. Take readings at least every five minutes and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the tip of the probe at the first sampling point and start the pump. Sample proportionally throughout the run. At the conclusion of each run, turn off the pump and record the final readings. Remove the probe from the stack and disconnect it from the train. Drain the ice bath and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes.

4.2 Sample recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a polyethylene shipment bottle. Rinse the three midget impingers and the connecting tubes with distilled water and add these washings to the same storage container.

4.3 Sample analysis. Transfer the contents of the storage container to a 50 ml. volumetric flask. Dilute to the mark with deionized, distilled water. Pipette a 10 ml. aliquot of this solution into a 125 ml. Erlenmeyer flask. Add 40 ml. of isopropanol and two to four drops of thorin indicator. Titrate to a pink endpoint using 0.01 N barium perchlorate. Run a blank with each series of samples.

5. *Calibration.*

5.1 Use standard methods and equipment which have been approved by the Administrator to calibrate the rotameter, pitot tube, dry gas meter, and probe heater.

5.2 Standardize the barium perchlorate against 25 ml. of standard sulfuric acid containing 100 ml. of isopropanol.

6. *Calculations.*

6.1 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (70° F. and 29.92 inches Hg) by using equation 6-1.

$$V_{m_{std}}=V_m\left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right)=17.71\frac{°R}{\text{in. Hg}}\left(\frac{V_m P_{bar}}{T_m}\right) \qquad \text{equation 6-1}$$

where:

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} = Absolute temperature at standard conditions, 530° R.

T_m = Average dry gas meter temperature, °R.

P_{bar} = Barometric pressure at the orifice meter, inches Hg.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.2 Sulfur dioxide concentration.

$$C_{SO_2}=\left(7.05\times10^{-5}\frac{\text{lb.-l.}}{\text{g.-ml.}}\right)\frac{(V_t-V_{tb})N\left(\frac{V_{soln}}{V_a}\right)}{V_{m_{std}}} \qquad \text{equation 6-2}$$

where:

C_{SO_2} = Concentration of sulfur dioxide at standard conditions, dry basis, lb./cu. ft.

7.05×10^{-5} = Conversion factor, including the number of grams per gram equivalent of sulfur dioxide (32 g./g.-eq.), 453.6 g./lb., and 1,000 ml./l., lb.-l./g.-ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml.

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

N = Normality of barium perchlorate titrant, g.-eq./l.

V_{soln} = Total solution volume of sulfur dioxide, 50 ml.

V_a = Volume of sample aliquot titrated, ml.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft., see Equation 6-1.

7. *References.*

Atmospheric Emissions from Sulfuric Acid Manufacturing Processes, U.S. DHEW, PHS, Division of Air Pollution, Public Health Service Publication No. 999-AP-13, Cincinnati, Ohio, 1965.

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Patton, W. F. and J. A. Brink, Jr., New Equipment and Techniques for Sampling Chemical Process Gases, J. Air Pollution Control Association, *13*, 162 (1963).

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide. are measure colorimetrically using the phenoldisulfonic acid (PDS) procedure.

1.2 Applicability. This method is applicable for the measurement of nitrogen oxides from stationary sources only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. *Apparatus*.

2.1 Sampling. See Figure 7-1.

2.1.1 Probe—Pyrex[1] glass, heated, with filter to remove particulate matter. Heating is unnecessary if the probe remains dry during the purging period.

2.1.2 Collection flask—Two-liter, Pyrex,[1] round bottom with short neck and 24/40 standard taper opening, protected against implosion or breakage.

2.1.3 Flask valve—T-bore stopcock connected to a 24/40 standard taper joint.

2.1.4 Temperature gauge—Dial-type thermometer, or equivalent, capable of measuring 2° F. intervals from 25° to 125° F.

2.1.5 Vacuum line—Tubing capable of withstanding a vacuum of 3 inches Hg absolute pressure, with "T" connection and T-bore stopcock, or equivalent.

2.1.6 Pressure gauge—U-tube manometer, 36 inches, with 0.1-inch divisions, or equivalent.

2.1.7 Pump—Capable of producing a vacuum of 3 inches Hg absolute pressure.

2.1.8 Squeeze bulb—One way.

2.2 Sample recovery.

2.2.1 Pipette or dropper.

2.2.2 Glass storage containers—Cushioned for shipping.

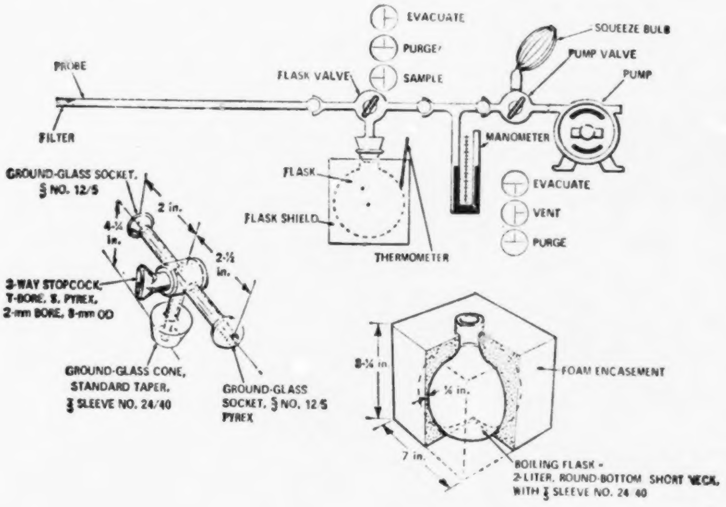
EVACUATE
PURGE
SAMPLE
SQUEEZE BULB
PUMP VALVE
PUMP
PROBE
FLASK VALVE
FILTER
MANOMETER
FLASK
FLASK SHIELD
THERMOMETER
EVACUATE
VENT
PURGE
GROUND-GLASS SOCKET, § NO. 12/5
2 in.
4-¼ in.
2-½ in.
3-WAY STOPCOCK, T-BORE, § PYREX, 2-mm BORE, 8-mm OD
GROUND-GLASS CONE, STANDARD TAPER, § SLEEVE NO. 24/40
GROUND-GLASS SOCKET, § NO. 12/5 PYREX
8-¼ in.
¼ in.
FOAM ENCASEMENT
7 in.
BOILING FLASK - 2-LITER, ROUND-BOTTOM SHORT NECK, WITH § SLEEVE NO. 24/40

Figure 7-1. Sampling train, flask valve, and flask.

2.2.3 Glass wash bottle.

2.3 Analysis.

2.3.1 Steam bath.

2.3.2 Beakers or casseroles—250 ml., one for each sample and standard (blank).

2.3.3 Volumetric pipettes—1, 2, and 10 ml.

2.3.4 Transfer pipette—10 ml. with 0.1 ml. divisions.

2.3.5 Volumetric flask—100 ml., one for each sample, and 1,000 ml. for the standard (blank).

2.3.6 Spectrophotometer—To measure absorbance at 420 nm.

2.3.7 Graduated cylinder—100 ml. with 1.0 ml. divisions.

2.3.8 Analytical balance—To measure to 0.1 mg.

3. *Reagents*.

3.1 Sampling.

3.1.1 Absorbing solution—Add 2.8 ml. of concentrated H_2SO_4 to 1 liter of distilled water. Mix well and add 6 ml. of 3 percent hydrogen peroxide. Prepare a fresh solution weekly and do not expose to extreme heat or direct sunlight.

3.2 Sample recovery.

3.2.1 Sodium hydroxide (1*N*)—Dissolve 40 g. NaOH in distilled water and dilute to 1 liter.

3.2.2 Red litmus paper.

3.2.3 Water—Deionized, distilled.

3.3 Analysis.

3.3.1 Fuming sulfuric acid—15 to 18% by weight free sulfur trioxide.

3.3.2 Phenol—White solid reagent grade.

3.3.3 Sulfuric acid—Concentrated reagent grade.

3.3.4 Standard solution—Dissolve 0.5495 g. potassium nitrate (KNO_3) in distilled water and dilute to 1 liter. For the working standard solution, dilute 10 ml. of the resulting solution to 100 ml. with distilled water. One ml. of the working standard solution is equivalent to 25 μg. nitrogen dioxide.

3.3.5 Water—Deionized, distilled.

3.3.6 Phenoldisulfonic acid solution—Dissolve 25 g. of pure white phenol in 150 ml. concentrated sulfuric acid on a steam bath. Cool, add 75 ml. fuming sulfuric acid, and heat at 100° C. for 2 hours. Store in a dark, stoppered bottle.

4. *Procedure*.

4.1 Sampling.

4.1.1 Pipette 25 ml. of absorbing solution into a sample flask. Insert the flask valve stopper into the flask with the valve in the "purge" position. Assemble the sampling train as shown in Figure 7-1 and place the probe at the sampling point. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuate the flask to at least 3 inches Hg absolute pressure. Turn the pump valve to its "vent" position and turn off the pump. Check the manometer for any fluctuation in the mercury level. If there is a visible change over the span of one minute, check for leaks. Record the initial volume, temperature, and barometric pressure. Turn the flask valve to its "purge" position, and then do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and flask valve area, heat the probe and purge until the condensation disappears. Then turn the pump valve to its "vent" position. Turn the flask valve to its "sample" position and allow sample to enter the flask for about 15 seconds. After collecting the sample, turn the flask valve to its "purge" position and disconnect the flask from the sampling train. Shake the flask for 5 minutes.

4.2 Sample recovery.

4.2.1 Let the flask set for a minimum of 16 hours and then shake the contents for 2 minutes. Connect the flask to a mercury filled U-tube manometer, open the valve from the flask to the manometer, and record the flask pressure and temperature along with the barometric pressure. Transfer the flask contents to a container for shipment or to a 250 ml. beaker for analysis. Rinse the flask with two portions of distilled water (approximately 10 ml.) and add rinse water to the sample. For a blank use 25 ml. of absorbing solution and the same volume of distilled water as used in rinsing the flask. Prior to shipping or analysis, add sodium hydroxide (1*N*) dropwise into both the sample and the blank until alkaline to litmus paper (about 25 to 35 drops in each).

4.3 Analysis.

4.3.1 If the sample has been shipped in a container, transfer the contents to a 250 ml. beaker using a small amount of distilled water. Evaporate the solution to dryness on a steam bath and then cool. Add 2 ml. phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a glass rod. Make sure the solution contacts all the residue. Add 1 ml. distilled water and four drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Cool, add 20 ml. distilled water, mix well by stirring, and add concentrated ammonium hydroxide dropwise with constant stirring until alkaline to litmus paper. Transfer the solution to a 100 ml. volumetric flask and wash the beaker three times with 4 to 5 ml. portions of distilled water. Dilute to the mark and mix thoroughly. If the sample contains solids, transfer a portion of the solution to a clean, dry centrifuge tube, and centrifuge, or filter a portion of the solution. Measure the absorbance of each sample at 420 nm. using the blank solution as a zero. Dilute the sample and the blank with a suitable amount of distilled water if absorbance falls outside the range of calibration.

5. *Calibration*.

5.1 Flask volume. Assemble the flask and flask valve and fill with water to the stopcock. Measure the volume of water to ±10 ml. Number and record the volume on the flask.

5.2 Spectrophotometer. Add 0.0 to 16.0 ml. of standard solution to a series of beakers. To each beaker add 25 ml. of absorbing solution and add sodium hydroxide (1*N*) dropwise until alkaline to litmus paper (about 25 to 35 drops). Follow the analysis procedure of section 4.3 to collect enough data to draw a calibration curve of concentration in μg. NO_2 per sample versus absorbance.

6. *Calculations*.

6.1 Sample volume.

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[1] Trade name.

$$V_{sc}=\frac{T_{std}(V_f-V_a)}{P_{std}}\left(\frac{P_f}{T_f}-\frac{P_i}{T_i}\right)=\left(17.71\ \frac{°\text{R}}{\text{in. Hg}}\right)(V_f-25\text{ ml.})\left(\frac{P_f}{T_f}-\frac{P_i}{T_i}\right)\quad\text{Equation 7-1}$$

where:

V_{sc} = Sample volume at standard conditions (dry basis), ml.

T_{std} = Absolute temperature at standard conditions, 530° R.

P_{std} = Pressure at standard conditions, 29.92 inches Hg.

V_f = Volume of flask and valve, ml.

V_a = Volume of absorbing solution, 25 ml.

P_f = Final absolute pressure of flask, inches Hg.

P_i = Initial absolute pressure of flask, inches Hg.

T_f = Final absolute temperature of flask, °R.

T_i = Initial absolute temperature of flask, °R.

6.2 Sample concentration. Read μg. NO_2 for each sample from the plot of μg. NO_2 versus absorbance.

$$C=\left(\frac{m}{V_{sc}}\right)\left(\frac{\frac{1\text{ lb.}}{\text{cu. ft.}}}{1.6\times10^{4}\frac{\mu\text{g.}}{\text{ml.}}}\right)=\left(6.2\times10^{-5}\frac{\text{lb./s.c.f.}}{\mu\text{g./ml.}}\right)\left(\frac{m}{V_{sc}}\right)\quad\text{equation 7-2}$$

where:

C = Concentration of NO_x as NO (dry basis), lb./s.c.f.

m = Mass of NO_2 in gas sample, μg.

V_{sc} = Sample volume at standard conditions (dry basis), ml.

7. *References.*

Standard Methods of Chemical Analysis. 6th ed. New York, D. Van Nostrand Co., Inc., 1962, vol. 1, p. 329–330.

Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure), In: 1968 Book of ASTM Standards, Part 23, Philadelphia, Pa. 1968, ASTM Designation D–1608–60, p. 725–729.

Jacob, M. B., The Chemical Analysis of Air Pollutants. New York, N.Y., Interscience Publishers, Inc., 1960, vol. 10, p. 351–356.

METHOD 8—DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. A gas sample is extracted from a sampling point in the stack and the acid mist including sulfur trioxide is separated from sulfur dioxide. Both fractions are measured separately by the barium-thorin titration method.

1.2 Applicability. This method is applicable to determination of sulfuric acid mist (including sulfur trioxide) and sulfur dioxide from stationary sources only when specified by the test procedures for determining compliance with the New Source Performance Standards.

2. *Apparatus.*

2.1 Sampling. See Figure 8-1. Many of the design specifications of this sampling train are de ribed in APTD–0581.

2.1.1 Nozzle—Stainless steel (316) with sharp, tapered leading edge.

2.1.2 Probe—Pyrex[1] glass with a heating system to prevent visible condensation during sampling.

2.1.3 Pitot tube—Type S, or equivalent, attached to probe to monitor stack gas velocity.

2.1.4 Filter holder—Pyrex[1] glass.

2.1.5 Impingers—Four as shown in Figure 8-1. The first and third are of the Greenburg-Smith design with standard tip. The second and fourth are of the Greenburg-Smith design, modified by replacing the standard tip with a ½-inch ID glass tube extending to one-half inch from the bottom of the impinger flask. Similar collection systems, which have been approved by the Administrator, may be used.

2.1.6 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 5° F., dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume.

2.1.7 Barometer—To measure atmospheric pressure to ±0.1 inch Hg.

2.2 Sample recovery.

2.2.1 Wash bottles—Two.

2.2.2 Graduated cylinders—250 ml., 500 ml.

2.2.3 Glass sample storage containers.

2.2.4 Graduated cylinder—250 ml.

2.3 Analysis.

2.3.1 Pipette—25 ml., 100 ml.

2.3.2 Burette—50 ml.

2.3.3 Erlenmeyer flask—250 ml.

2.3.4 Graduated cylinder—100 ml.

2.3.5 Trip balance—300 g. capacity, to measure to ±0.05 g.

2.3.6 Dropping bottle—to add indicator solution.

3. *Reagents.*

3.1 Sampling.

3.1.1 Filters—Glass fiber, MSA type 1106 BH, or equivalent, of a suitable size to fit in the filter holder.

3.1.2 Silica gel—Indicating type, 6–16 mesh, dried at 175° C. (350° F.) for 2 hours.

3.1.3 Water—Deionized, distilled.

3.1.4 Isopropanol, 80%—Mix 800 ml. of isopropanol with 200 ml. of deionized, distilled water.

3.1.5 Hydrogen peroxide, 3%—Dilute 100 ml. of 30% hydrogen peroxide to 1 liter with deionized, distilled water.

3.1.6 Crushed ice.

3.2 Sample recovery.

3.2.1 Water—Deionized, distilled.

3.2.2 Isopropanol, 80%.

3.3 Analysis.

3.3.1 Water—Deionized, distilled.

3.3.2 Isopropanol.

3.3.3 Thorin indicator—1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid, disodium salt (or equivalent). Dissolve 0.20 g. in 100 ml. distilled water.

3.3.4 Barium perchlorate (0.01*N*)—Dissolve 1.95 g. of barium perchlorate [$Ba(CO_4)_2 \cdot 3H_2O$] in 200 ml. distilled water and dilute to 1 liter with isopropanol. Standardize with sulfuric acid.

3.3.5 Sulfuric acid standard (0.01*N*)—Purchase or standardize to ±0.0002 *N* against 0.01 *N* NaOH which has previously been standardized against primary standard potassium acid phthalate.

4. *Procedure.*

4.1 Sampling.

4.1.1 After selecting the sampling site and the minimum number of sampling points, determine the stack pressure, temperature, moisture, and range of velocity head.

4.1.2 Preparation of collection train. Place 100 ml. of 80% isopropanol in the first impinger, 100 ml. of 3% hydrogen peroxide in both the second and third impingers, and about 200 g. of silica gel in the fourth impinger. Retain a portion of the reagents for use as blank solutions. Assemble the train without the probe as shown in Figure 8-1 with the filter between the first and second impingers. Leak check the sampling train at the sampling site by plugging the inlet to the first impinger and pulling a 15-inch Hg vacuum. A leakage rate not in excess of 0.02 c.f.m. at a vacuum of 15 inches Hg is acceptable. Attach the probe and turn on the probe heating system. Adjust the probe heater setting during sampling to prevent any visible condensation. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 70° F. or less.

4.1.3 Train operation. For each run, record the data required on the example sheet shown in Figure 8-2. Take readings at each sampling point at least every 5 minutes and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Start the pump and immediately adjust the flow to isokinetic conditions. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the

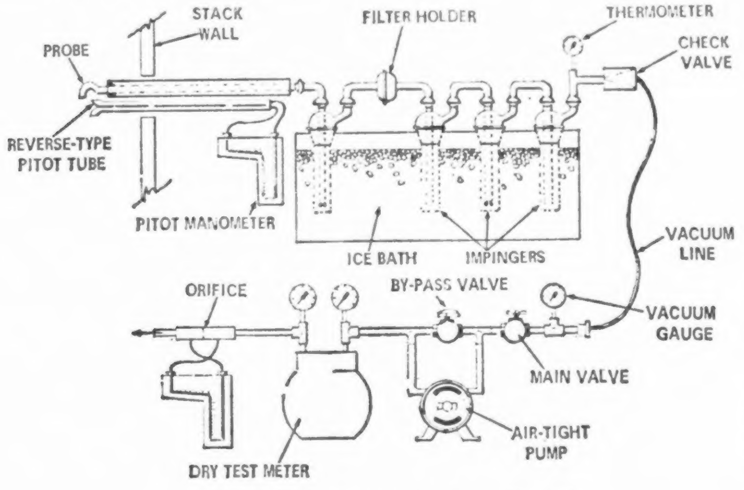

Figure 8-1. Sulfuric acid mist sampling train.

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[1] Trade name

rapid adjustment of the sampling rate without other computations. APTD-0576 details the procedure for using these nomographs. At the conclusion of each run, turn off the pump and record the final readings. Remove the probe from the stack and disconnect it from the train. Drain the ice bath and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes.

PLANT__________
LOCATION__________
OPERATOR__________
DATE__________
RUN NO.__________
SAMPLE BOX NO.__________
METER BOX NO.__________
METER ΔH@__________
C FACTOR__________

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE__________
BAROMETRIC PRESSURE__________
ASSUMED MOISTURE, %__________
HEATER BOX SETTING__________
PROBE LENGTH, m.__________
NOZZLE DIAMETER, in.__________
PROBE HEATER SETTING__________

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STATIC PRESSURE (P_S), in. Hg	STACK TEMPERATURE (T_S), °F	VELOCITY HEAD (ΔP_S),	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER (ΔH), in. H_2O	GAS SAMPLE VOLUME (V_m), ft³	GAS SAMPLE TEMPERATURE AT DRY GAS METER		SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE °F
							INLET ($T_{m_{in}}$), °F	OUTLET ($T_{m_{out}}$), °F		
TOTAL										
AVERAGE							Avg	Avg		
							Avg.			

Figure 8-2. Field data.

4.2 Sample recovery.

4.2.1 Transfer the isopropanol from the first impinger to a 250 ml. graduated cylinder. Rinse the probe, first impinger, and all connecting glassware before the filter with 80% isopropanol. Add the rinse solution to the cylinder. Dilute to 250 ml. with 80% isopropanol. Add the filter to the solution, mix, and transfer to a suitable storage container. Transfer the solution from the second and third impingers to a 500 ml. graduated cylinder. Rinse all glassware between the filter and silica gel impinger with deionized, distilled water and add this rinse water to the cylinder. Dilute to a volume of 500 ml. with deionized, distilled water. Transfer the solution to a suitable storage container.

4.3 Analysis.

4.3.1 Shake the container holding isopropanol and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample. Pipette a 100 ml. aliquot of sample into a 250 ml. Erlenmeyer flask and add 2 to 4 drops of thorin indicator. Titrate the sample with barium perchlorate to a pink end point. Make sure to record volumes. Repeat the titration with a second aliquot of sample. Shake the container holding the contents of the second and third impingers. Pipette a 25 ml. aliquot of sample into a 250 ml. Erlenmeyer flask. Add 100 ml. of isopropanol and 2 to 4 drops of thorin indicator. Titrate the sample with barium perchlorate to a pink end point. Repeat the titration with a second aliquot of sample. Titrate the blanks in the same manner as the samples.

5. *Calibration.*

5.1 Use standard methods and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, dry gas meter, and probe heater.

5.2 Standardize the barium perchlorate with 25 ml. of standard sulfuric acid containing 100 ml. of isopropanol.

6. *Calculations.*

6.1 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (70° F., 29.92 inches Hg) by using Equation 8-1.

$$V_{m_{std}}=V_m\left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{P_{std}}\right)=\left(17.71\frac{°R}{\text{in. Hg}}\right)V_m\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{T_m}\right)$$

equation 8-1

where:

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} = Absolute temperature at standard conditions, 530° R.

T_m = Average dry gas meter temperature, °R.

P_{bar} = Barometric pressure at the orifice meter, inches Hg.

ΔH = Pressure drop across the orifice meter, inches H_2O.

13.6 = Specific gravity of mercury.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.2 Sulfuric acid concentration.

$$C_{H_2SO_4}=\left(1.08\times10^{-4}\frac{\text{lb.-l.}}{\text{g.-ml.}}\right)\frac{(V_t-V_{tb})(\underline{N})\left(\frac{V_{soln}}{V_a}\right)}{V_{m_{std}}}$$

equation 8-2

$C_{H_2SO_4}$ = Concentration of sulfuric acid at standard conditions, dry basis, lb./cu. ft.

1.08×10^{-4} = Conversion factor including the number of grams per gram equivalent of sulfuric acid (49 g./g.-eq.), 453.6 g./lb., and 1,000 ml./l., lb.-l./g.-ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml.

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

N = Normality of barium perchlorate titrant, g.-eq./l.

V_{soln} = Total solution volume of sulfuric acid (first impinger and filter), ml.

V_a = Volume of sample aliquot titrated, ml.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft., see Equation 8-1.

6.3 Sulfur dioxide concentration.

$$C_{SO_2}=\left(7.05\times10^{-5}\frac{\text{lb.-l.}}{\text{g.-ml.}}\right)\frac{(V_t-V_{tb})(\underline{N})\left(\frac{V_{soln}}{V_a}\right)}{V_{m_{std}}}$$

equation 8-3

where:

C_{SO_2} = Concentration of sulfur dioxide at standard conditions, dry basis, lb./cu. ft.

7.05×10^{-5} = Conversion factor including the number of grams per gram equivalent of sulfur dioxide (32 g./g.-eq.) 453.6 g./lb., and 1,000 ml./l., lb.-l./g.-ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml.

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

N = Normality of barium perchlorate titrant, g.-eq./l.

V_{soln} = Total solution volume of sulfur dioxide (second and third impingers), ml.

V_a = Volume of sample aliquot titrated, ml.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft., see Equation 8-1.

7. *References.*

Atmospheric Emissions from Sulfuric Acid Manufacturing Processes, U.S. DHEW, PHS, Division of Air Pollution, Public Health Service Publication No. 999-AP-13, Cincinnati, Ohio, 1965.

Corbett, D. F., The Determination of SO_2 and SO_3 in Flue Gases, Journal of the Institute of Fuel, 24:237-243, 1961.

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METHOD 9—VISUAL DETERMINATION OF THE OPACITY OF EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. The relative opacity of an emission from a stationary source is determined visually by a qualified observer.

1.2 Applicability. This method is applicable for the determination of the relative opacity of visible emissions from stationary sources only when specified by test procedures for determining compliance with the New Source Performance Standards.

2. *Procedure.*

2.1 The qualified observer stands at approximately two stack heights, but not more than a quarter of a mile from the base of the stack with the sun to his back. From a vantage point perpendicular to the plume, the observer studies the point of greatest opacity in the plume. The data required in Figure 9-1 is recorded every 15 to 30 seconds to the nearest 5% opacity. A minimum of 25 readings is taken.

3. *Qualifications.*

3.1 To certify as an observer, a candidate must complete a smokereading course conducted by EPA, or equivalent; in order to certify the candidate must assign opacity readings in 5% increments to 25 different black plumes and 25 different white plumes, with an error not to exceed 15 percent on any one reading and an average error not to exceed 7.5 percent in each category. The smoke generator used to qualify the observers must be equipped with a calibrated smoke indicator or light transmission meter located in the source stack if the smoke generator is to determine the actual opacity of the emissions. All qualified observers must pass this test every 6 months in order to remain certified.

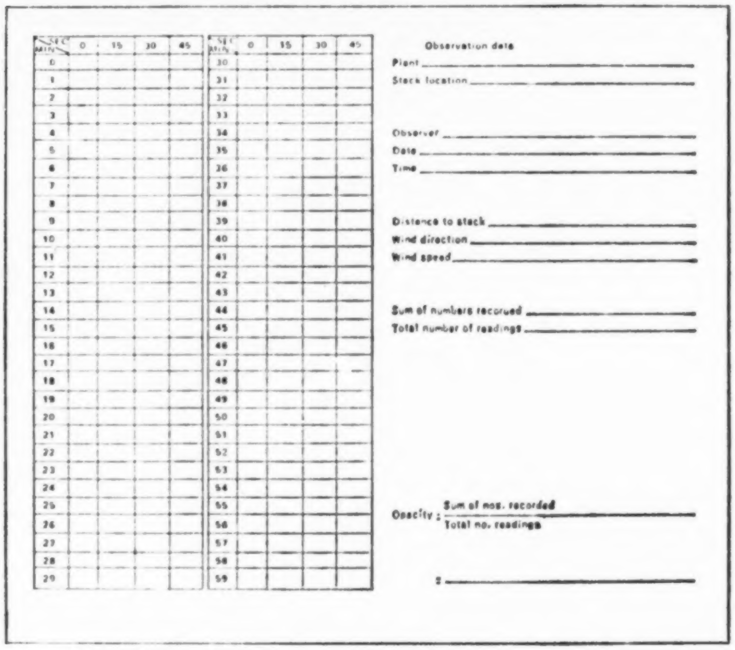
4. *Calculations.*

4.1 Determine the average opacity.

5. *References.*

Air Pollution Control District Rules and Regulations, Los Angeles County Air Pollution Control District, Chapter 2, Schedule 6, Regulation 4, Prohibition, Rule 50, 17 p.

Kudluk, Rudolf, Ringelmann Smoke Chart, U.S. Department of Interior, Bureau of Mines, Information Circular No. 8333, May 1967.



SEC / MIN	0	15	30	45	SEC / MIN	0	15	30	45
0					30				
1					31				
2					32				
3					33				
4					34				
5					35				
6					36				
7					37				
8					38				
9					39				
10					40				
11					41				
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16					46				
17					47				
18					48				
19					49				
20					50				
21					51				
22					52				
23					53				
24					54				
25					55				
26					56				
27					57				
28					58				
29					59				

Observation data

Plant ______

Stack location ______

Observer ______

Date ______

Time ______

Distance to stack ______

Wind direction ______

Wind speed ______

Sum of numbers recorded ______

Total number of readings ______

Opacity = $\frac{\text{Sum of nos. recorded}}{\text{Total no. readings}}$

= ______

Figure 9-1. Field data.

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